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Final Report on Investigation of Transferable Technology for Application in Peat Dewatering Research

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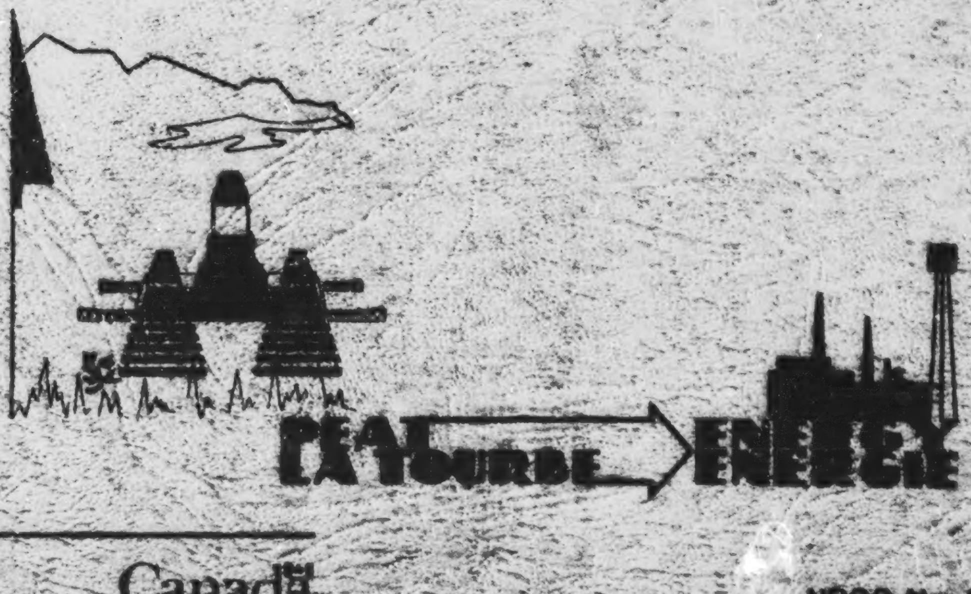

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FINAL REPORT ON
INVESTIGATION OF TRANSFERABLE TECHNOLOGY FOR APPLICATION IN PEAT DEWATERING RESEARCH

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This study was undertaken in partial fulfillment of Canada's role as an active member of the International Energy Agency (IEA). The project contract was awarded as a result of an unsolicited proposal to the Manager of the Peat Program, National Research Council of Canada.

The contractors contacted over 400 personnel during the course of the study. Almost without exception these people responded promptly, and with genuine interest and cooperation. The enthusiastic sharing of information and insights, together with suggestions regarding further sources of information, enabled the contractors to synthesize and correlate material from a multitude of disciplines.

Special appreciation is given to those researchers who shared both their knowledge and their time, and who were free to discuss this and their own projects during sometimes lengthy interviews.

The contractors also wish to acknowledge the cooperation and communication with the project's Scientific Authority, John Sheppard; the Manager of the Peat Program, Ted Tibbetts; and Ralph Overend, Manager of the Bioenergy Program; all under the National Research Council of Canada.

EXECUTIVE SUMMARY

The project described in this report was initiated in response to a concern recognized and expressed by the International Energy Agency, in which Canada is a member. Fuel-quality peat is found in abundance throughout the world's temperate zone; its use as a fuel is limited by its high moisture content of up to or greater than 90 percent (wet basis). Artificial dewatering technologies presently used on a commercial scale are able to economically remove peat water only to the 75 percent (w.b.) level; further dewatering uses more energy than it releases. Peat dewatering studies, while becoming more sophisticated, have not yet produced sufficient data to provide researchers with a clear understanding of the components or character of peats. Neither are the fundamental mechanisms of dewatering fully understood.

This study was designed to survey and document research that is being done, or that has been completed, in areas where the research methods or results hold potential for transfer to the dewatering of peat. Over 400 research personnel were contacted; government, industry, and university sections were fully represented. Extensive literature searches and reviews were carried out; discussions were held with professionals by telephone and in person. Analysis of the acquired data indicated those areas most

relevant to the study; primary researchers readily became apparent.

The report reflects the methodology used by the researchers to attain the project objectives, which were:

- identification of disciplines and subdisciplines in which research work may be transferable to future studies in the fundamental aspects of peat dewatering,
- identification of transferable research results and research methods from each relevant discipline or sub-discipline,
- identification of researchers in universities, government agencies, and companies who have done or are currently doing relevant or transferable research,
- provision of a brief explanation of the transferable research as it relates to gaps in knowledge concerning the fundamental aspects of peat dewatering.

The contractors, in identifying research carried out in other fields, and gaps in current knowledge directly related to peat technology, classified the thrust of the project search requirements in the broad areas of:

- State-of-the-Art: Fundamental Aspects of Peat Dewatering
- Microbiology of Peat
- Porous Media Studies
- Physical Chemistry: Principles Actions and Characterization
- Cellulose - Lignin Degradation
- Research on Water-Binding Mechanisms
- Drying Measurements and Modelling

The search for transferable technologies led to examination of work in very diverse fields. The need to examine methods of pore characterization led to primary inquiries in civil engineering, petroleum engineering, physics and chemical engineering. Chemical characterization needs were met in the pulp and paper, textile, and food industries; and in basic chemical research. Movement of fluids in porous media is being researched in civil engineering, chemical engineering, petroleum engineering, and agricultural engineering. The nature of water-holding mechanisms is being studied in fields where high moisture content materials are handled such as agricultural engineering (livestock wastes), mineral engineering (cakes and slurries), chemical engineering (sanitary wastes), and the food industry (drying and preservation of food). Microbial studies are being carried out in biology and chemical engineering departments and forestry research centres.

The search for relevant transferable technologies revealed that:

- Biological and microbially produced compounds could play a significant role in evolving more effective peat dewatering procedures. Changes in the chemical structure of peat may change water-holding capacity.
- Surface chemistry studies have direct application to fundamental research on the way in which water is held in peat.
- Well-established methods for characterization and quantification of pore space are available for use in peat studies with minimal adaptation. The conceptual framework for development and testing of models of pore configuration and fluid flow has been established. Use of these models will require adaptation and further empirical studies to provide the basis for verification.
- Characterization of the peat, followed by application of principles used by scientists for other media, will help produce the data required for a comprehensive peat dewatering research program.
- Studies on degradation of peat constitutents, chiefly lignin and cellulose, may have indirect benefit in developing innovative dewatering methods.
- Interest in identifying water-holding mechanisms and assessing their relative importance is evident in

several disciplines. Basic studies have revealed promising techniques for detection and analysis. Many of these studies, however, are still in preliminary stages.

- Theoretical and experimental work is being conducted on drying of hygroscopic materials. Modelling and measuring techniques are available that could appropriately be transferred to peat research.

The research subjects, methods, and results examined during the project are fully documented in the report. The study has been strongly inter-disciplinary; as a result, it has brought together information from all relevant scientific and technological areas. The depth and array of information available for the use of peat researchers is clearly identified. The task of priorizing and selecting specific research subjects now belongs to the respective bodies under whose auspices this study was conducted.

RÉSUMÉ ADMINISTRATIF

Le projet décrit dans le présent rapport fait suite à un problème reconnu et exprimé par l'Agence internationale de l'énergie dont le Canada fait partie. On trouve en abondance, dans toutes les zones tempérées du globe, de la tourbe de qualité combustible; l'emploi de la tourbe comme combustible est limité par sa teneur élevée en eau, qui peut atteindre ou dépasser 90 % (du poids mouillé). Les méthodes artificielles de séchage actuellement utilisées à l'échelle commerciale ne permettent d'extraire l'eau de la tourbe de façon rentable que jusqu'à 75 % (du poids mouillé); pour enlever davantage d'eau, on doit utiliser plus d'énergie que la tourbe n'en libère. Les études sur le séchage de la tourbe, bien que devenant plus sophistiquées, n'ont pas encore produit suffisamment de résultats, pour donner aux chercheurs une meilleure compréhension des composants ou du caractère des tourbes. On comprend mal aussi les mécanismes fondamentaux du séchage.

On a conçu cette étude pour passer en revue et documenter la recherche réalisée actuellement ou déjà complétée, dans les domaines où les méthodes ou les résultats de la recherche pourraient s'appliquer aux procédés de séchage de la tourbe. Plus de 400 chercheurs ont été contactés; le gouvernement, l'industrie et les secteurs universitaires étaient pleinement représentés. Des études et examens détaillées de la documentation ont été faits. Des discussions ont eu lieu avec les spécialistes, par téléphone

ou en leur présence. L'analyse des données obtenues a indiqué les domaines qui se rapportaient le plus à l'étude; on a rapidement identifié les chercheurs qui seraient le plus utiles.

Le rapport décrit la méthode suivie par les chercheurs pour atteindre les objectifs du projet, à savoir :

- l'identification des disciplines et sous-disciplines dans lesquelles les travaux de recherche pourraient s'appliquer plus tard aux études sur les aspects fondamentaux du séchage de la tourbe.
- l'identification des résultats et méthodes de recherche applicables, tirés de toute discipline ou sous-discipline en rapport avec l'étude,
- l'identification des chercheurs provenant des universités, des organismes gouvernementaux et des compagnies qui ont effectué ou effectuent actuellement des recherches pertinentes ou applicables.
- une brève explication sur la recherche applicable, dans la mesure où ceci permet de combler des lacunes de nos connaissances concernant les détails fondamentaux du séchage de la tourbe.

Les adjudicataires, cherchant à identifier la recherche effectuée dans d'autres domaines, et les lacunes de nos connaissances se rapportant aux méthodes de traitement des tourbes, ont classé suivant leur orientation générale les exigences en matière de recherche dans le cadre du projet, comme suit :

- état actuel de la technologie : aspects fondamentaux du séchage de la tourbe
- microbiologie de la tourbe
- études des milieux poreux
- chimie physique : principes, actions et caractérisation
- dégradation de la lignine et de la cellulose
- recherche sur les mécanismes de liaison avec l'eau
- mesures et modélisation des processus de séchage

La recherche de technologies qui soient applicables nous a amenés à examiner les travaux effectués dans des domaines très divers. En raison du besoin d'examiner les méthodes de détermination de la porosité, on a entrepris des études fondamentales en génie civil, en génie pétrolier, en physique et en génie chimique. On a obtenu les détails chimiques nécessaires dans des études venant de l'industrie des pâtes et papiers, de l'industrie textile, et des industries alimentaires; et grâce à la recherche chimique fondamentale. On étudie actuellement le mouvement des fluides à l'intérieur des milieux poreux, dans les secteurs suivants : génie civil, génie chimique, génie pétrolier et génie agricole. Actuellement, on étudie la nature des mécanismes de liaison avec l'eau dans les domaines où l'on emploie des produits fortement hydratés, par exemple en génie agricole (fumier de bestiaux), génie minier (dépôts de boue et coulis), génie chimique (eaux usées sanitaires), et industrie alimentaire (séchage et conservation des aliments). Les départements de biologie et de génie chimique et les centres de recherche forestière réalisent actuellement des études microbiologiques. La recherche de techniques appropriées, se prêtant à des applications, a indiqué que :

- Les composés biologiques produits par l'activité microbienne pourraient dans une mesure importante servir à la mise au point de procédés plus efficaces de séchage de la tourbe. Des modifications de la structure chimique de la tourbe permettraient de changer la capacité de rétention d'eau de celle-ci.
- Les études relatives à la chimie des surfaces peuvent être directement appliquées à la recherche fondamentale sur les mécanismes de rétention de l'eau par la tourbe.
- Il existe des méthodes reconnues de détermination et mesure de la porosité, que l'on peut appliquer aux études sur les tourbes avec un degré minimum d'adaptation. On a déjà établi le cadre théorique de mise au point et d'expérimentation des modèles de porosité et de circulation des fluides. Pour pouvoir employer ces modèles, on devra adapter la recherche et poursuivre les études empiriques, de façon à disposer d'un mode de vérification des résultats.
- La caractérisation de la tourbe, suivie de l'application des principes qu'utilisent les chercheurs pour

étudier d'autres types de produits, aidera à obtenir les données nécessaires à la réalisation d'un programme détaillé de recherche sur le séchage de la tourbe.

- Les études sur la décomposition des constituants de la tourbe, surtout de la lignine et de la cellulose, pourraient indirectement servir à la mise au point de méthodes nouvelles de séchage de la tourbe.
- Dans plusieurs disciplines, se manifeste un intérêt évident pour les mécanismes de liaison avec l'eau, et pour l'évaluation de leur importance relative. Des études fondamentales ont permis d'envisager des techniques prometteuses de détection et d'analyse. Toutefois, un grand nombre de ces études en sont encore aux étapes préliminaires.
- On effectue actuellement des études théoriques et expérimentales sur le séchage des matières hygroscopiques. On dispose de techniques de modélisation et de mesure qui pourraient facilement s'appliquer à la recherche sur les tourbes.

Dans ce rapport, on décrit en détail les thèmes et méthodes de recherche, et les résultats examinés dans le cadre du projet. Cette étude a un caractère fortement interdisciplinaire; de ce fait, elle a permis de réunir l'information recueillie dans tous les secteurs scientifiques et technologiques pertinents. On a clairement identifié la portée et la gamme des informations utiles aux chercheurs étudiant la tourbe. Il reste maintenant aux organismes respectifs, sous les auspices desquels a été réalisée cette étude, à classer et sélectionner les thèmes spécifiques de recherche.

1.0 INTRODUCTION

1.1 Background

The Canadian Peat Program of the National Research Council of Canada (NRCC) has sponsored and administered fundamental and applied research programs that have contributed to development of peat as an energy resource. The findings of these research programs are disseminated nationally and internationally. Through active membership in the International Energy Agency (IEA) and the International Peat Society (IPS), NRCC is able to plan and execute cooperative research programs and gain rapid access to research work completed in other peat-producing countries.

The project described in this report was initiated in response to a concern expressed by several IEA country representatives that a comprehensive program to investigate peat dewatering problems was needed. This project, as further discussed in Sections 1.4 and 1.5, emphasizes the technology transfer of principles, techniques and methods that may be applicable to peat dewatering. The National Energy Administration of Sweden is conducting a three-year project entitled "Basic Studies of Water-Binding in Peat". Progress reports on that project are regularly submitted to the IEA; project findings are, therefore, not discussed in this report.

In situ peat can contain 90 percent water (wet basis) or more. Drying of fuel peat by addition of heat in large quantities is not an energy efficient process. Mechanical pressing operations are energy efficient but do not remove sufficient water. Representatives of the IEA concluded that the most effective way to tackle the peat dewatering problem was to investigate the way in which water is held in peat, so that water removal technologies could be improved. Research work of this type requires a very comprehensive physico-chemical investigation of peat. Prior to initiating this type of program, careful research planning was required. As part of the planning process, the authors of this report were asked to identify in-progress or completed research work that could be applied to this research effort.

1.2 Fuel Peat Characteristics

Peat that is considered desirable for fuel use is more decomposed than peats used for horticultural purposes. On the von Post decomposition (humification) scale of H_1 to H_{10}, fuel peats have a value of H_3 or greater, which indicates that the peat can range from slightly decomposed to completely decomposed. The peat in these H ranges must also have a high bulk density, low ash content, high caloric value and low level of toxic substances. Monenco Ontario Ltd. (1981, p. 19) in a study prepared for the Ontario Ministry of Natural Resources, characterized fuel peat according to its chemical analysis, caloric value, combustion characteristics, and other properties. The published tables are reproduced below:

Chemical Analyses	
Carbon %	50 - 60
Hydrogen %	5.0 - 6.5
Oxygen %	30 - 40
Nitrogen %	1.0 - 2.5
Sulfur %	0.1 - 0.2

Caloric Value	
Heat value at 40% water content kcal/kg	2500 - 3000
Heat value at 60% water content kcal/kg	1780 - 1960
Heat value of dry peat kcal/kg	4700 - 5100

Combustion Characteristics	
Ash Content %	2 - 10
Melting Point of Ash °C	1100 - 1200
Volatiles %	60 - 70

Other Properties	
Bulk Density at 50% moisture content kg/m3	300 - 400
pH	4 - 8
In situ water content (% by wet weight)	80 - 92
Fibre content (% by wet weight)	10 - 60

Fuel peats and lignites have similar chemical compositions, combustion characteristics and caloric values.

1.3 Project Objectives

The objectives of this project were:

- identification of disciplines and subdisciplines in which research work is done that may be transferable to future studies in the fundamental aspects of peat dewatering,
- identification of research results and research methods from each relevant discipline or subdiscipline that may be transferable,
- identification of researchers in universities, government agencies, and companies who have done or are currently doing transferable research,
- provision of a brief explanation of the transferable research as it relates to gaps in knowledge concerning the fundamental aspects of peat dewatering.

1.4 Project Scope

The search for transferable research was restricted to topics that could be applied to research on water retention in peat, and how it could be expelled more effectively than current methods allow. The emphasis in all cases was to find research results and research methods that could be effectively used. There were no geographic restrictions placed on the searching process.

Research into mechanical dewatering methods was not considered in this study unless the work was related to a physico-chemical investigation. Similarly, biomass fuel technologies that do not involve direct combustion were considered only if initial steps in these processes merit further investigation on the basis of their alteration of the peat-water relationship.

1.5 Project Emphasis

The emphasis in researching relevant technologies was placed on those aspects of peat dewatering that likely will require that most concentrated research efforts in the future. Major areas were determined to be characterization of the porous structure and analysis of flow phenomena, investigation of microbial activity, understanding physical chemistry principles and effects, investigation of degradation of peat constituents and identification of water-holding mechanisms.

In all cases, the search for transferable technology included research aimed at discovering or clarifying basic relationships, as well as research aimed at quantification and prediction of behavior.

1.6 Methodology

Appropriate disciplines and subdisciplines, and the researchers in those fields, were ascertained by several methods. Initially, the literature on peat dewatering was examined, to define major gaps in knowledge. Preliminary lists of disciplines and subdisciplines that could provide insight on each of these topics were compiled. Computer literature searches on appropriate aspects of each of these subject areas were completed. This phase of the project was supplemented by leads obtained from manual literature searching. Personal contact and correspondence with researchers whose work was discovered from these searches produced many more leads.

The most applicable research papers and reports were obtained from the individual researchers or from libraries or technical dissemination organizations such as the National Technical Information Service (NTIS) or the Canada Institute for Scientific and Technical Information (CISTI). The contents of the documents were analyzed in relation to the peat dewatering problem.

The final step in the analysis process was to visit Canadian and American research facilities, where transferable research was in progress or had been recently completed. Interviews with principal researchers were structured to define the impetus for initiating the research, the initial hypotheses and methods of inquiry, research results obtained and their implications with respect to further study, and finally the applicability of the researcher's work to peat dewatering work.

1.7 Relevant Technologies

The search for transferable technologies led to examination of work in very diverse fields. The need to examine methods of pore characterization led to primary inquiries in civil engineering,, petroleum engineering, physics and chemical engineering. Chemical characterization methods were examined in the pulp and paper, textile and food industries and in basic chemical research. Movement of fluids in porous media is being researched in civil engineering, chemical engineering, petroleum engineering, and agricultural engineering. The nature of water-holding mechanisms is being studied in fields where high moisture content materials are handled such as agricultural engineering (livestock wastes), mineral engineering (cakes and slurries), chemical engineering (sanitary wastes), and the food industry (drying and preservation of food). Microbial studies are being carried out in biology and chemical engineering departments and forestry research centres.

1.8 Report Organization

The second section of this report provides an overview of the current state of knowledge on the fundamental aspects of peat dewatering and points out major gaps in this knowledge. Section 3 consists of a state-of-the-art report on peat microbiology. The remainder of the report describes research work for which cross-disciplinary expertise could be applied to narrowing the research gaps previously identified in Section 2.

2.0 STATE-OF-THE-ART: FUNDAMENTAL ASPECTS OF PEAT DEWATERING

2.1 Problem Definition

Peat is known even to the general public as a material with very good water-holding capabilities. Its reputation in this regard comes from the commercial success in marketing peat moss as a soil improvement material for gardening. Basic research on how or why peat is such an efficient water-holding material, however, has not progressed very far. Current interest in this topic is spurred by a need to develop affordable dewatering technology for the use of peat as fuel.

In situ peat commonly has a moisture content of 90 percent or greater (as a percent of wet weight). To use peat as a fuel on a commercially viable basis, the moisture content must be reduced to a maximum of about 50 percent. In other words, an in situ peat sample of 10 kg may contain up to 9 kg of water. Conversion of such a material to that of a usable energy resource necessitates the removal of 8 kg of water from the original 10 kg total weight sample. The remaining 2 kg would consist of 1 kg each of peat and of water; i.e. 50 percent moisture content (w.b.) (Kopstein, 1979). If peat is to be used as a commercially viable fuel, water removal must be a cost-effective and energy-efficient process.

In order to meet these objectives, it is necessary to obtain a better understanding, through fundamental research, of how and why water is held in peat.

2.2 Water Retention Characteristics

It is important to identify the basic water-holding mechanisms in peat. A plethora of classification systems have been developed to describe water-holding mechanisms in soils (Rode, 1969). Some of these systems contain so many subdivisions that they are unwieldy to use, due to the difficulty in understanding the differences between mechanisms. The simpler systems are helpful in gaining a better understanding of the water-holding processes at work, but it is difficult to draw firm boundaries on where one mechanism's effect dominates over others. These systems do not address interaction of water-holding mechanisms.

Kandebo (1982) used a simple classification scheme for water retention in peats that is quite appropriate to the present state of knowledge on the topic. Water held in peat was described as follows:

- physically entrapped water: water retained by pore networks within the fibrous structure and within cells of plant material
- adsorbed water: water held to molecules in peat by weak bonds such as hydrogen bonds or by electrostatic attraction

- chemically bonded water: water which is part of the chemical structure of the peat.

This system is based primarily upon the work of Hannel (1923), Fuchsman (1980), and Rohrer (1980).

2.2.1 Rewetting of Peat

When peat is air- or oven-dried, it is impossible to rewet the sample to its original water content even if the sample is soaked in water for long periods of time. The sample volume also shrinks upon drying and cannot be restored to initial size during rewetting. These phenomena have puzzled both researchers, and horticultural peat producers who sell their products by volume. van Dijk reported that the low volume was attributable to the poor wettability of dry peat. Other researchers have tried to explain why dry peat is so unwettable. Page (1921) suggested that it was due to adsorbed air on the dry solid peat material. Hudig and Redlich (as reported in van Dijk) hypothesized that films of iron humate coated the dry peat.

These researchers also suggested the presence of waxes, fats and resins. Fuchsman (1980) has also suggested that waxes may coat the particle surfaces during the drying process.

van Dijk (1971) argued that drying of peat caused the formation of secondary bonds, which he described as "hydrogen bridges". He felt that these bonds were too strong to be dissolved by water. He found that swelling of peat upon rewetting could be enhanced by replacing hydrogen ions or polyvalent cations with alkali or ammonium ions. van Dijk (1971) found that well-humified peats shrink more upon drying than less humified ones do. When water was reintroduced, swelling was very limited, often less than 10 percent of the original volume. He hypothesized that the behavior of the well-humified peats was due to the properties of the colloidal humic fraction in these peats.

Kandebo (1982) was also interested in learning more about why dried peat is difficult to rewet. Of particular interest to him was testing of the hypothesis that drying causes some of the pore network to collapse, thus leaving less space available for water to occupy [(Graves (1980), Rohrer (1980), Punwani (1980)]. To test this hypothesis, he dried samples in a constant humidity chamber to water contents ranging from about 80 to 30 percent. Samples were then broken up, rewetted with distilled water and left in a sealed jar for a week. Samples were allowed to drain for a few minutes before final water content determinations were made. It was readily apparent that when peat water content dropped below 60 percent, reversible rewetting was not possible.

Freeze-drying tests on peat provided a further test of the pore collapse hypothesis. Freeze-drying is a popular method of preparing porous specimens for microscopic examination because it causes minimal disturbance to the original pore structure. The freeze-dried samples can be rewetted without difficulty. Results of freeze-drying tests provide very strong support for the pore collapse hypothesis.

Another important observation made during the freeze-drying tests was that even under very carefully controlled drying procedures, 2 to 5 percent of the water could not be removed. Kandebo concluded that this water was held by chemical bonds that were not broken by freeze-drying but could be broken by heating. Samples with about 5 percent water remaining were the more humified North Carolina peats. Kandebo (1982) conducted a series of tests to explore the role of bitumens (waxes and resinous materials) in the peat-water relationship. As Fuchsman (1980) pointed out, bitumens can be dissolved in organic liquids and can, therefore, be easily extracted from peat samples. Fuchsman also pointed out that bitumens can provide a water-repellent coating on peat particles, particularly when heating occurs. Kandebo felt that if bitumens are able to keep water away from pores, they can also enable the escape of water already in the pores. The investigators wanted to find out if it were easier to remove water by mechanical means from peat after bitumen removal. Solvents (e.g. DMSO, DMF, THF and CS_2) were used to remove bitumen. Each sample was broken up and shaken and left soaking in one of the solvents for ten days. Peat samples and excess solvents were then separated. The samples were centrifuged, peat-solvent separation was attempted and moisture content determinations were made. The results were inconclusive because it was apparent that the solvents had leached additional substances from the peat. Three of the solvents produced an unidentified dark brown and purple liquid. The solid phase could be described as dark and oily, far removed from the original peat consistency. In one instance, contact with CS_2 produced a white waxy substance which fit the "water repellent" description provided by Fuchsman. Unfortunately, attempts to repeat this result were unsuccessful. The only conclusion that could be reached from this series of tests was that since moisture content did not change appreciably during centrifuging, the substances leached by the solvents did not alter the water-holding capabilities of the peat except in the case of the waxy, white substance. Further conclusions could likely have been drawn if either the leached substance(s) or the altered peat solids had been assayed.

2.2.2 Studies on Physically Entrapped Water

Studies by Puustjarvi, as reported by Monenco Ontario Ltd., indicated that sphagnum mosses have leaves that contain hyaline cells with oval-shaped cavities lined with lignins. Until this cell structure is substantially degraded by humification, water held in the cavities is trapped. An additional study on how plant structure affects water retention in peat is being carried out by Cohen at Los Alamos National Laboratory. The results of this study were not available to the public at the time that this report was prepared. The study, when complete, will provide information on a wider range of plant material in fuel peats.

The extent of capillary retention of water depends upon the characteristics of both the wetting liquid and the capillary surface. Water is pushed into the capillaries by a pressure gradient at the air-water interface. There is no indication in the literature on how much of the water in peats is held in capillaries or enclosed voids. Data on capillary size is scarce. Volarovich and Churaev (1968) reported that capillaries and other small openings in peat were 0.3 to 20 μm in width. Opportunities for water to be held in capillaries decreases with humification as the pore structure of the plant material is gradually destroyed. Puustjarvi, as reported in Monenco Ontario Ltd. (1981), was able to predict pore volume as a percentage of total sample volume from the von Post humification number. In fresh peats (H_1 to H_3), pore volumes of 95 to 97 percent were to be expected. These peats had a high permeability. Capillary retention of water was very important. Peat particle sizes were generally greater than 0.1 mm. As humification increased to H to H_6, pore volume decreased to 92 to 94 percent. Capillary held water was still very important.

S.W. Kandebo (1982), an M.S. student who was supervised by Dr. D. Graves, Department of Chemical Engineering, University of Pennsylvania, undertook a series of experiments to investigate water-holding mechanisms in capillaries. They were interested in evaluating the appropriateness of two capillary models. They first described capillaries as thin tubes with a hemispherical drop at one end. A simple relationship between liquid density, tube radius, tube length, surface tension and gravitational force was derived based on physics principles. The result indicated that gravitational force is inversely proportional to the weight of water retained in a capillary. Further analysis indicated that a centrifugal force ten times that of normal gravity would drain 90 percent of capillary water. If surface tension were lowered, the capillary could be emptied of liquid more easily.

Testing of this hypothesis required use of microfilters and centrifuging of samples. Sample weight was initially checked every hour, then every twenty minutes.

Although the amount of water removed by centrifuging was not as great as had been predicted, the capillary shape model held up well under scrutiny.

A second model did not describe capillary shape as well. It was the "ink bottle" concept described by Adamson (1967). Kandebo (1982) hypothesized that ink bottle-shaped capillaries could be drained more completely if they were randomly sliced. He used a blender to approximate random slicing. He was able to get peat samples "sliced" to different extents by varying the blender speed. Dewatering capability was not enhanced until peat was agitated at the highest speed for 30 minutes. Since normal domestic procedures done with a blender are completed in much shorter times, it must be concluded that extremely violent agitation is required to "slice" peat tissue. The investigator also concluded that the ink bottle concept was not valid. If it were a correct description of peat pore networks, he would have expected greater increases in dewatering capability with less agitation.

2.2.3 Studies on Adsorbed Water

Kandebo (1982) performed preliminary investigations on water retention by adsorption. He looked particularly at the possibility of hydrogen bonding and ionic attraction. Two peat samples were used in these experiments: one was a highly decomposed North Carolina peat; the other was a less decomposed Minnesota peat. Peat samples were treated with urea, a substance known to disrupt hydrogen bonding; or with sodium iodide, a material used to disrupt ionic attraction. Data presented indicate that relatively undecomposed peats treated with urea released 33 percent more water than did untreated peats in the sample. The investigators concluded that hydrogen bonding is, in part, responsible for water retention in peat. On the other hand, only a 12 percent increase in water release was produced by similar treatment of the highly decomposed North Carolina peat. Experiments using peats from these same samples measured water removal subsequent to treatment with sodium iodide. The resultant data indicate no significant difference in water removal capacities, between sodium iodide treated and untreated peats, in either the highly decomposed or the relatively undecomposed states.

Volarovich and Churaev (1968) found that physically and chemically bound water in peats was adsorbed by active organic groups. The indicated sources for the energy of adsorption were van der Waal's forces or hydrogen bonding; energy measured ranged from 0.1 to 0.3 up to 5 to 10 kcal/mol. Thermodynamic data has not been gathered in sufficient quantity to provide greater detail.

2.2.4 Studies on Chemically Bonded Water

To gain an appreciation of chemical bonding of water in fuel peat, it is necessary to study the colloidal structure of the peat material. In highly humified (H_7 to H_{10}) peats, colloidal retention is the dominant water-holding mechanism. Van Dijk (1971) described the humic matter in peats as "coiled, long chain molecules, two or three dimensional cross-linked macromolecules or reversible aggregates of such molecules [which], may be present as more or less swollen, loosely built structures". He also indicated that charged particles can exist virtually anywhere within this structure rather than only on the surface. These charges are due to ionization of acid or basic groups within the colloidal structure. Overall size may be expanded due to repulsion between groups with like charges or shrunk due to attraction of oppositely charged groups. Volarovich and Churaev (1968) characterized peat as "a complex, heterogeneous, polydispersed system". They reported that it contained solutions, hydrophobic soils and hydrophylic semi-colloids. They found that the colloidal structure depended heavily on the chemical composition of compounds formed as the peat decomposes. They concluded by using electron microscopy, that hydrophylic behavior of low moor peats was more heavily dependent on pH and composition. In contrast, high moor peats have a large quantity of hydrophylic humic material. As decomposition proceeds in both types of peats, the amount of hydrophobic humic material increases.

Colloidal size studies on peats have been carried out primarily by Russian investigators. Churaev, as reported by van Dijk (1971), determined that particle sizes ranged from 0.2 to 1 μm. Churaev found that the humic matter he tested contained micro-aggregates. Particle size measurements made by electron microscopy have indicated radii of 60 to 100 Å (van Dijk, 1971). Molecular weight values show an even greater scatter, 2 000 to 20 000. This spread is attributed to a lack of consensus on the correct experimental method. Visser (1963) found that molecular weight and particle shape change with humification.

Humic matter in soils can be subdivided into humic acids which are soluble in alkali solutions and can be reprecipitated in an acid solution. This material is generally found to fall in the colloidal size range. Fulvic acid, which cannot be reprecipitated in this manner, has a particle size range less than that normally attributed to colloids. Humic matter in this smaller size range has received little attention from peat researchers. Because studies on the colloidal structure of peat are not very comprehensive at present, little has been published on colloidal water-binding mechanisms in peat.

2.3 Water Removal Techniques

This section briefly describes water removal techniques that have been the subject of basic research. Conventional solar drying, thermal drying and mechanical pressing practices that are in widespread industrial use are not presented. The techniques described in this section are the result of preliminary laboratory testing or pilot studies. Some have proven to be successful on a small scale, some have produced inconclusive results and others have proven to be useless. Microbial tests are described in Section 3.0.

2.3.1 Physical Research

2.3.1.1 Addition of Processed Peat. Peat dewatering in Bavaria has been enhanced by adding dried powdered peat at up to 40 percent water content. The raw peat was then pressed to achieve a 60 percent water content. Drying reduced the water content further to 15 percent. This technique is thought to alter the colloidal structure of the peat in the initial pressing operation (Tsaros,1980).

2.3.1.2 Addition of Coal or Coal/Lignite Mixtures. At the Jet Propulsion Laboratory, California Institute of Technology, preliminary attempts were made to add coal and/or lignite with or without acid to peat. Coal particle size ranging from 8 to 35 mesh sizes were introduced with no apparent success. Ratios of peat to coal ranged from 1 to 10 (Hsu, 1984).

2.3.1.3 Centrifuging. Kandebo (1982) conducted a number of centrifuging experiments on peats from Minnesota and North Carolina. For relatively undecomposed peats from Minnesota, centrifuging removed about 26 percent of the water. In highly decomposed North Carolina peats, about 14 percent was removed. The investigators had great difficulty in interpreting this data because they could not determine how much of the initial water in the samples was retained in capillaries. They were able to determine very readily that most of the water expelled during centrifuging came out at low relative centrifugal force values. It was also possible to use the data obtained from these tests as a standard from which the effectiveness of chemical dewatering schemes could be compared.

At the Royal Institute of Technology in Sweden, centrifuge studies have been carried out since 1976. Slurried peat having 3 to 7 percent dry matter is dewatered in a decanter-centrifuge. Fines smaller than 10 µm are removed. The remaining peat has about 15 to 17 percent dry matter. It is then dewatered in a mechanical press until about 30 percent of the material is dry. Further water removal by heating is carried out. The fines in the effluent from the first dewatering step are flocculated with iron sulfate and polyelectrolytes. The flocculated peat is then pressed and heated (Lindström, Hörnell and Lindström, 1980).

2.3.1.4 Saturation Effects. Kandebo (1982) compared the dewatering capability of saturated peats versus unsaturated ones. He found that unsaturated samples are easier to dewater by centrifuging. He suggested that this is due to the colloidal structure of saturated peat.

2.3.1.5 Sample Location (Depth). Kandebo investigated the effect of location (depth) within a deposit on dewatering characteristics. Similar dewatering behavior was exhibited regardless of the depth from which the sample came.

2.3.1.6 Innovative Mechanical Testing. At the Institute of Gas Technology, an internal rotary compression system has been tested on a bench scale and is currently undergoing prototype tests. The system allows simultaneous compression and shear. On a bench scale, samples could be dewatered to 40 percent moisture content. Results of prototype testing are not available at this time (IGT 1984).

2.3.2 Chemical Research

2.3.2.1 Electro-osmosis. Electro-osmotic dewatering was performed in Germany. An electric current was passed through the peat in an attempt to separate peat solids from water. Two factors acted against its success: it required more electrical energy than most mechanical dewatering systems, and it was not possible to reduce water content below a value of about 70 percent (Tsaros, 1980). Electro-osmotic dewatering of in situ peat has also been tried with varying degrees of success by geotechnical engineers. Their conclusions on economic viability have been similar to those of the German researchers.

2.3.2.2 Use of Solvents. Solvent extraction experiments have been conducted by the Institute of Gas Technology under U.S. Department of Energy (DOE) sponsorship. The mechanism being exploited is that water can be dissolved in certain solvents at appropriate temperatures. The solvent is subsequently decanted. This work is progressing at the laboratory scale only (Tsaros, 1980) due to the high cost of solvent for a full-scale operation.

Pore fluid removal tests were conducted by Kandebo (1982) using methanol as the solvent exchanger for water. The methanol saturated samples were subjected to centrifuging. The object of these tests was to determine whether a liquid with a lower surface tension than water could be expelled from water-saturated peat more readily than could water be expelled. The researchers found that it was easier to remove methanol than water from the peat samples by centrifuging. He noted, however, that at least part of the enhanced removal of pore fluid may have been due to methanol-induced leaching of one or more substances from the peat samples.

2.3.2.3 Use of Hydroxides and Chlorides. Attempts were made to change the colloidal structure of peat by subjecting the peat to alkaline solutions [0.1% $Ca(OH)_2$, 5% $CaCl_2$ and 5% NaOH] at 95°C for four hours. There was a slight gain rather than a loss in moisture in the tests conducted at the Jet Propulsion Laboratory at California Institute of Technology (Hsu, 1984).

Sharp (1982, 1983) at Memorial University of Newfoundland has been investigating the feasibility of using lime ($CaCO_3$) to raise the pH of the peat-water system to a value near the isoelectric point. He found that addition of the lime, and freezing and thawing of the peat samples tested, allowed mechanical dewatering to achieve 50 to 60 percent water removal in laboratory studies. Further investigation of the feasibility of using this method on a larger scale indicated that the lime would decrease the caloric value of the peat and increase the ash content to unacceptable levels.

2.3.2.4 Acid Hydrolysis. Sulfuric acid (10%) was added to peat at the Jet Propulsion Laboratory at California Institute of Technology at 95°C and held for 4 hours. There was a slight gain in moisture in the processed peat (Hsu, 1984).

2.3.2.5 Use of Surfactants. Reax (a sodium salt of lignosulfonate) and Fluorad F3-128(3M) were introduced as surfactants in peat dewatering trials at the Jet Propulsion Laboratory, California Institute of Technology. The moisture content of the samples increased slightly in all cases (Hsu, 1984).

Work undertaken by D.G. Cooper (1984), at McGill University, indicated that the organic material in fluid removed from peat can be used as a substrate to produce surfactants, polymers and enzymes. These dewatering agents, when reintroduced to peat samples, increased the amount of water removed, by subsequent pressing, up to 60 percent. Cooper's work is further discussed in Sections 3.3 and 5.3.3 of this report.

At the National Research Council of Canada, Atlantic Research Laboratory, Dr. L. Ayub and Mr. J. Sheppard have begun an investigation of water-holding mechanisms in fuel peat. The emphasis in this study is on the effects of cationic surfactants on peat dewatering. They are attempting to correlate zeta potential of the peat particles with surfactant concentration. Samples that have been dosed with surfactant will be dewatered by mechanical pressing. The effect of various surfactants will be compared with respect to dewatering enhancement and the cause of changes in the peat-water relationship.

2.3.2.6 Use of Supercritical Fluids. At the Jet Propulsion Laboratory, California Institute of Technology, preliminary dewatering trials using CO_2 at supercritical conditions (T = 35 - 40°C, P = 1100 - 1200 psi) were made. Only minor reductions in moisture content were observed in peat processed in this manner. When the processed peat was left overnight at ambient conditions, it did not dry as thoroughly as untreated peat would have.

It was hypothesized prior to testing that CO_2 at the supercritical point would rupture some of the peat particles and release physically trapped water.

2.3.2.7 Carbonization. A peat-water slurry is heated in a closed system to 200°C at 2.5 MPa. The object is to disrupt the colloidal structure of peat. Carbon dioxide and water are released. Reductions in oxygen content during wet carbonization enhance the caloric value of the peat. Peat treated in this manner can be mechanically dewatered to less than 50 percent

(Gallo and Sheppard, 1981). Development of a full-scale facility has been under negotiation in Scandinavia and the United States.

2.3.2.8 Wet Oxidation. At the Ontario Research Foundation, extensive work has been done on wet oxidation of peat. Two processes have been researched. The first completely oxidizes wet peat to produce energy in the form of steam and hot water. Since this process does not involve dewatering, it is not relevant to this review. The second process, however, involves partial oxidation of peat which results in an end product that is essentially the same as that produced by wet carbonization (see Section 2.3.2.7). The remaining material can be dewatered mechanically to a moisture content of 50 percent or less (Gallo and Sheppard, 1981).

3.0 MICROBIOLOGY OF PEAT

3.1 Introduction

The preceding section of this report contains a state-of-the-art report on peat dewatering. This section consists of a definition and elucidation of peat formation, and the existence and activity of microbial organisms in situ. The review articles of Given and Dickenson (1975), Kuster (1975) and the report or Cooper et al (1984) were used extensively in the preparation of this report. The data presented here is considered significant for several purposes: to summarize and present current knowledge of the subject matter; to identify gaps in our present understanding of the topic; to provide possible future researchers with a base from which to begin, to define the presence of microbial organisms so their activities may be specifically related to fuel peat characteristics; and to enable comparisons or transfers of technologies and expertise across disciplinary boundaries.

For the purpose of this section peats will be broadly grouped as either rheophilus, that is, nourished by nutrient-rich groundwater (also referred to as being mineratrophic); or ombrophilus, where formation is dependent on nutrient-poor rain water.

Many early scientists believed that peat lands were sterile. Investigations have shown, however, that many different types of microbes (i.e. bacteria and fungi), with a variety of physiological and biochemical activities, are present in peat.

Environmental factors, e.g. wetness, oxygen concentration, pH, temperature and nutrient status will determine the numbers, types and activities of micro-organisms present. The types, numbers and activities of microbes recorded also is very dependent on the methodology used. Techniques for numerical estimation range from those estimating viability, e.g. the plate count and most probable number techniques, which detect only those organisms that can grow under the nutrient and environmental conditions used, to those involving direct microscopic counts which enumerates both living and dead cells. The use of scanning electron microscopic techniques provides a means of determining the incidence of microbial cells on particulate surfaces; that is, the degree of colonization can be estimated from such procedures. All of these methods have been used in estimating the microbial numbers present in peats. Microbial activities, e.g. hydrolysis of polysaccharides, proteins, fats and pectins can be estimated via techniques which measure the clearing of opaque solutions or solid media containing these insoluble polymers. Mineralization studies (i.e. where carbon atoms in a compound are converted to CO_2) are very useful in studying the metabolism of compounds by micro-organisms particularly when molecules in the substrate contain radioactive carbon-14. All of these techniques have been used in studies on the activity of micro-organisms in peat.

3.2 Microbial Populations

3.2.1 Fungi

Studies on the distribution of numbers and types of microorganisms have yielded some interesting information particularly on the fungal flora of peats. Fungi found in acid peats include species of Cephalosporium, Cladosporium, Geotrichum, Mortierella, Mucor, Trichoderma and sterile dark and hyaline forms. Several of these fungi are felt to be restricted to these habitats as they are not usually found in mineral soils. Rheophilic fen habitats appear to have a greater diversity of fungi than do ombrotrophic sites. Some of the genera previously-mentioned are present. Isolates of Arthrinium, Cylindrocarpon, Fusarium, Pseudeurotium and Volutella genera also are commonly found in such environments.

Fungi are of primary importance in litter decay and are usually most abundant in the surface layers of peat. Usually, higher numbers of fungi are found in rheophilus peats than in ombrophilus systems. Numbers of fungal propagules (i.e. mycelial pieces, spores, etc. which will give rise to a colony which can be counted) vary from 10^3 to 10^5/g of peat. The direct measurement of the length of fungal hyphae gave values of 160 to 320 m/m^3 in two acid peats. This latter procedure indicates the presence of a much larger amount of fungal biomass than is obtained with the estimation of the number of fungal propagules.

3.2.2 Bacteria

Bacterial types found in peats represent aerobes (i.e. require oxygen for growth), anaerobes (i.e. do not require or are inhibited or killed by oxygen) and spore formers (i.e. produce a spore which is a viable body resistant to heat, desiccation, etc.). Members of the following genera have been reported in peats: *Achromobacter*, *Bacillus*, *Chromobacterium*, *Clostridium*, *Cytophaga*, *Micrococcus*, *Mycobacterium*, *Pseudomonas* and streptomycetes (*Actinomyces*, *Micromonospora*, *Nocardia* and *Streptomyces*).

The number of viable bacterial cells reported in peats varies widely; values ranging from 10^5 to 10^7 cells/g of peat when a non-selective media (i.e. a medium which is known to support the growth of a wide range of bacterial genera) and aerobic conditions were used. Direct microscopic methods (which do not differentiate between viable and non-viable cells) however, have yielded counts in the order of 10^9 cells/cm^3. Bacteria have been demonstrated to be present in all strata of ombrophilus and rheophilus peats. A decrease in aerobic organisms with increasing peat depth has been reported and the number of anaerobic bacteria were found to increase with increasing depth of peat sampled. This is to be expected, as environmental conditions change from aerobic to anaerobic with increasing depth of peat. In general, the data indicates that there is decreased presence of viable micro-organisms with increasing depth, although their presence has been observed in all strata by numerous investigators. Examination of particles from freshly exposed deep peat samples showed the presence of very fine mycelium, typical of actinomycetes, whereas thicker fungal mycelium and bacterial cells were absent. Individual bacterial cells, however, were numerous in interstitial waters between peat particles. It is possible that such cells are in a dormant (Stevenson, 1978) state (i.e. a resting state) because the environment is unfavorable for growth.

A comparison of enumeration data present in the literature is very difficult as different counting methods and experimental media were used and in some cases protocols were not published. In addition, different peats were used and they often were not characterized as to their physical-chemical properties, i.e. developmental status. Two major microbiological questions which have to be considered in enumerating bacteria in peat are:

a) What is the best basis for enumeration: number/g, $/cm^3$ or surface area.

b) For reporting fungal data, is the number of propagules or the length of mycelium the best method for estimating fungal presence in peat?

3.3 Microbial Activities

In order for micro-organisms to rapidly change the chemical composition of organic matter (and hence its physical properties), environmental conditions have to be able to sustain microbial growth. These conditions include a source of energy and cell carbon (i.e. the plant material), nitrogen and phosphate. The elemental requirements for growth, i.e. Ca^{++}, etc., are usually present in sufficient quantities. If aerobic growth is to take place, O_2 has to be present; otherwise conditions are only suitable for anaerobic growth. Aerobic activity is, however, many times more active in oxidizing organic matter (i.e. plant tissues) than is anaerobic metabolism. Hence in anaerobic environments, such as wetlands, the oxidation rate of organic matter will be slow even if all other factors are suitable for growth. It is also likely that the most readily utilizable organic components in the plant material will have been removed in the more active surface layers of the peat bog. Hence there will only be a relatively limited supply of readily oxidizable organic matter in the anaerobic deep strata of wetlands. The rate of change in the chemical composition of organic matter under such conditions is slow.

While micro-organisms can be recovered from all strata of peatlands, it is probable that fungi only play a major role in organic matter decomposition at the surface of peatlands, because of their aerobic nature. Bacteria, i.e. anaerobes, should be the most active group in the deeper strata of peatlands, providing environmental conditions are suitable for their growth.

Bacteria active in various aspects of the carbon cycle (i.e. cellulytic organisms), the nitrogen cycle (i.e. ammonifying organisms, nitrifying organisms, nitrate reducers and anaerobic but not aerobic nitrogen-fixing bacteria), and the sulfur cycle (i.e. sulfate reducers, thiosulfate oxidizers as well as a few sulfur oxidizers) have been reported to be present in peats. Photosynthetic bacteria (anaerobes) and methanogens also have been isolated along with methane-oxidizing bacteria. Such activities are compatible with a role for micro-organisms in the formation and transformation of peats. Bacterial isolates from peatlands recently (Williams and Crawford, 1983) have been shown to grow on various carbohydrates, aromatic compounds and hydrocarbons, suggests that the microbial population present is capable of oxidizing a wide range of organic materials. Some isolates also were able to mineralize ^{14}C-lignin and ^{14}C-sphagnum moss.

The numbers and potential activities of micro-organisms present in peat wetlands suggest that such flora could play a major role in the conversion of plant materials (usually wetland species) to peats. The normal conversion of such material via the carbon cycle to CO_2 and H_2O, however may be restricted by the environment in which peat accumulates. The wetness of the environment usually results in low oxygen concentrations (which means that rapid aerobic decomposition of organic matter cannot occur) and is usually accompanied by a low temperature and sometimes a low pH. Under such conditions microbial activity is slow. Recent studies (Williams and Crawford, 1983a) using pure bacterial isolates from ombrophilic peats showed that a lowering of the temperature from 30^{o}C to 4^{o}C slowed but did not halt microbial activity. Williams and Crawford also observed that activity was greater at ambient pH's (3 to 4.5) than at neutral pH's. Decreasing the oxygen concentration, however, did significantly reduce activity of such isolates. The concentrations of the nutrients nitrogen and phosphorus did not appear to be a limiting factor in determining microbial activities.

While microbial activity undoubtedly plays a role in the conversion of fresh plant material to peat, their role in the further maturation of peat is unknown at present. It would appear to be limited by the environmental conditions present. In particular, the lack of oxygen in deeper peat strata would limit microbial activity to that involving anaerobic species. The presence of microbes in all strata of peat, however, suggests that the potential for activity is there. Aquatic studies (Hobbie, 1979) have shown that while microbial numbers may vary only one order of magnitude, biochemical activity measurements may vary over four orders of magnitude. Thus, only a small amount of growth may be required to product significant changes in the chemical and hence the physical properties of natural substances such as peat.

The relationship between microbial growth and the resultant chemical-physical properties of peat such as water-holding capacity has yet to be established. Cooper (1984) reports that as the humus content (humic acids and their derivatives, rich in phenolics and carboxylic acid groups) of peat increases, the ability to remove water by mechanical processes decreases. This condition he interprets as being due to the colloidal properties of humus which is dispersed in a continuous lattice throughout the aqueous phase. Thus, the higher the humus content of a peat, the more the peat is resistant to mechanical dewatering.

The type and quantity of the inorganic ions present can also have an effect on the stability of peat water. Given and Dickenson in their review article (p. 138) reported that the Russian workers, Volarovich and Churaev observed that the addition of Ca^{++} or other polyvalent ions to peat colloids immobilized peat water, whereas increasing the Na^{+} or K^{+} content liberated water.

Cooper (1984) also suggests that the waxy residues in peat (bitumens), which have been shown to retard water penetration of peat particles, may also prevent the removal of water during dewatering processes. He investigated the effects of biological products on a mechanical dewatering process. Substances added were: a chitosan salt (a charged polymer of a commercially available biological structural material) which aids in the coagulation of peat particles; microbial surface active compounds (e.g. surfactin) which reduce interfacial and/or surface tension of peat water; or lipases (lipolytic enzymes) which hydrolyze the waxy coating surrounding peat particles. All of these additions increased the amount of water removed from peat by mechanical means over that observed from peat samples not receiving these treatments.

It was also observed by Cooper (1984) that less solids were lost in the pressate when biological products were included in the dewatering process. The pressed water, with the addition of a few nutrients, sustained the growth of micro-organisms which yielded products useful in the dewatering process or other industries.

3.4 Conclusions

Microbial activity plays a dominant role in the conversion of plant debris to peat and undoubtedly is involved in the processes where peat changes from highly structured plant material to humus, which has no regular shape. Such changes in the chemical structure of peat must have an affect on its physical properties such as water-holding capacity.

The water-holding capacity of peat undoubtedly results from the interaction of products of the microbial decomposition of plant materials, e.g. colloids with chemicals, in particular divalent cations, in incursion waters. However, there is no data in the literature which clearly supports such an hypothesis. There is a direct relation, however, between the changes in the chemical composition of oil brought about by microbial activity and the resultant physical properties of the oil (Westlake, 1982). It is reasonable to assume that a similar relationship occurs in the microbial decomposition of peat.

4.0 POROUS MEDIA STUDIES

4.1 Introduction

In attempting to understand the peat-water relationship, it is necessary to be able to describe the porous networks in peat and to describe the movement of water through them. Typical pore size and shape data needs to be obtained. Hypotheses on the configuration of pore networks must be developed and tested. Movement of water, gases and ions within the porous networks must be investigated. The following sections describe principles, investigative methods and current research that may be transferable to peat dewatering research.

4.2 Pore Space Characterization

4.2.1 Observation of Pore Space

Soil fabric refers to the arrangement of soil particles and pore space in a soil. Microfabric denotes structure that cannot be seen with the naked eye. By the 1950's, equipment to allow direct observation of soil fabric became available. Research by soil scientists and geotechnical engineers was aimed primarily at understanding clay particle arrangement and its effect on engineering and agricultural uses. In the 1960's, soil fabric research became more prevalent because sample preparation techniques had been improved and the scanning electron microscope had been developed. By 1970, interest in studying other soils began, with sand, gravel and silt being popular choices (Mitchell 1976).

Microfabric studies have been carried out on peat but their emphasis has, for the most part, been on plant origin determination, classification or correlation of engineering behavior with particle arrangement. Equipment and personnel to carry out soil microfabric investigations are found in many universities, government and private research laboratories. In Canada, the Geotechnical Research Centre headed by Dr. Raymond Yong at McGill University, and the Geotechnical Research Group of the Civil Engineering Department at the University of Western Ontario under the direction of Dr. Robert M. Quigley, have conducted soil microfabric studies for many years. The University of California at Berkeley, Department of Civil Engineering (Dr. J.K. Mitchell) has developed an excellent reputation in soil fabric studies in the United States as has the Civil Engineering Department at the University of Michigan (Dr. D.H. Gray).

Methods of observation of pore space are described in Sections 4.2.1.1, to 4.2.1.3.

4.2.1.1 Optical Microscopy. Optical microscopy is useful in observing individual particles or pore spaces of silt size or larger (Mitchell 1976). Optical microscope images can be viewed through the microscope eyepiece or may be projected on a ground glass screen. The image may be photographed, or an electronic image may be obtained with a television camera. Analysis of electronic images may be accomplished with analyzers (Kaye 1981).

Soil scientists took an earlier interest in studying peat structure by optical microscopy. Their aim following World War II was to determine the position of peat in the rapidly evolving agricultural soil classification systems. They were also interested in the formation of peats.

Dr. Gerhard B. Lee of the University of Wisconsin Department of Soil Science, Madison Wisconsin has done soil fabric analysis using optical microscopy. He found that thin sections could be prepared by impregnating peat cores with Carbowax, then cutting and polishing the specimen. Carbowax produced little or no structural changes. Peat water could be gradually replaced by Carbowax after submersion for three to five days (Lee, 1965). This technique was also used by J.K. Mitchell, Department of Civil Engineering, University of California, Berkeley, in moist inorganic clay studies (Mitchell, 1956).

Dr. Arthur Cohen, a geologist who works regularly in peat, coal and lignite research, is using optical microscopy to estimate porosity, fibre and mineral contents at Los Alamos National Laboratory. In cooperation with the Institute of Gas Technology, he is currently studying samples that have been dewatered to various water contents to see if he can discover any correlation between pore size and distribution and ease of dewatering. He has used a 1.5 m cube of peat encased in a 100 mesh box. The samples are fixed in alcohol, acetic acid and formaldehyde and dehydrated in ethanol and tertiary butyl alcohol (Cohen, 1983).

4.2.1.2 Electron Microscopy. Electron microscopy is a useful technique for observation of particles or pore spaces smaller than 1 μm. Transmission electron microscopes produce images through use of electromagnetic lenses. Three dimensional observations may be made by a technique called shadow casting. The shadow is created by metal vapor in a vacuum. The size of the shadow indicates the size of the third dimension. Scanning electron microscopes (SEM) use a beam of electrons that move in a scanning pattern directed onto the specimen to be examined. The specimen and electron beam are in a vacuum. When the electron beam reaches the specimen, secondary electrons are generated. The secondary electrons are collected in a detector. The image from an SEM is generated by line scan procedures. Signals from an SEM can be fed directly to a computer for analysis by line scan techniques of the three-dimensional appearing SEM images.

A few SEM studies have already been completed on peat. They have not analyzed pore space in the level of detail required for a fundamental dewatering study. Sample preparation techniques, however, are well established.

In 1976, P.E. Pheeney, a civil engineer with undergraduate training and hands-on experience in botanical research, did an M.Sc.

thesis at the University of New Brunswick on peat fabric and its relationship to geotechnical behavior under Dr. A.O. Landva. His study was done in cooperation with the U.N.B. Department of Biology. The department's research efforts since that time on peat have been aimed at developing geotechnical testing equipment rather than on soil fabric studies. The studies were confined to sedge and Sphagnum peats at various stages of decomposition. Pheeney used both optical and scanning electron microscopy as research tools. Optical microscopy was done by Pheeney on dispersed, sieved peat. He determined that it was possible to determine the number of stems and leaves, and to determine their porosity. Colloidal material is lost in the sieving process and addition of a dispersing agent changes surface forces. It is possible to observe the behavior of the +200 sieve material during drying by this method.

SEM studies were done after samples were prepared by oven-drying, air-drying or critical point drying. This technique permitted allowed pore space characterization but did not allow study at various stages in the drying process.

Landva and Pheeney (1980) made several interesting observations:

a) water surrounding each leaf evaporated before cellular water disappeared (optical studies).

b) amorphous peat (highly decomposed) showed little change in fabric when compressed (SEM studies).

c) void size ranges and porosities could be calculated for the peats studied. Porosities were calculated.

d) highly decomposed peats should be prepared for SEM study by freeze-drying.

Further study on a wide variety of peats with observations by optical and electron microscopy would provide more comprehensive data on peat porosity. SEM sample preparation by freeze-drying or critical point drying would be more appropriate than either oven- or air-drying to minimize pore shrinkage (Mitchell, 1976).

Dr. A.W. Dhowian of the Civil Engineering Department, University of Riyadh, Saudi Arabia, did a Ph.D. thesis at the University of Wisconsin, Madison, on consolidation behavior of peat. His thesis supervisor was Dr. Tuncer B. Edil in the Civil Engineering Department. Dhowian studied scanning electron micrographs of four Wisconsin peats and attempted to relate the laboratory results to changes in peat structure during compression. His microstructure observations were less quantitative than Pheeney's because the primary emphasis of the Wisconsin study was on macroscopic behavior. He did make two important observations (Dhowian and Edil, 1981):

a) the peats he studied had a system of both macro and micropores,

b) void ratio was more important in determining compression behavior than peat type was.

4.2.1.3 Image Analysis. Manual determination of pore size or distribution would be a very time-consuming tedious task. Various devices for automated evaluation of microscopy images have been available since the early 1950's. The early devices were linescan logic systems. In the 1960's, image analysis was accomplished by interfacing television cameras with digital computers; this technology is still in use. By the mid-1970's, solid state, low-cost image digitizers became available; most of which can be programmed by the operator to perform extra functions (Kaye, 1981).

Image analyzers are currently being used to determine pore size, shape and distribution in a dewatering study on fine coal that is being conducted at the University of Pittsburgh, Department of Chemical and Petroleum Engineering.

To store and use information on peat particle/pore boundaries in a computer system, the location of boundaries must be recorded in a systematic, yet accurate fashion. For highly convoluted or rugged boundaries such as those found in peat, special techniques are required. Mandelbrot (1978) has developed the concept of fractal analysis. Kaye (1981) has applied this concept to description of the shape of irregular fine particles. It involves essentially a random walk estimate of the perimeter of a particle or pore space. Fractal analysis is being used successfully in pore space characterization studies on fine coal at the University of Pittsburgh.

4.2.2 Pore Size Distribution

4.2.2.1 Intrusion of Non-Wetting Fluids. Forced intrusion of a non-wetting fluid is a useful technique to investigate pore size distribution when the pore sizes range from about 0.01 to 10 μm. Mercury is usually used as the non-wetting fluid. The pressure required to force a non-wetting liquid into a pore is related to the diameter of the pore. The total volume of fluid intruded into a sample at each pressure level represents the pore volume occupied by pores of a particular diameter. The analysis assumes an idealized cylindrical pore. Mitchell (1976) pointed out several limitations to this method. They are:

- the pores must be dry prior to testing. In peats, this means that the sample must be freeze-dried to preserve the original pore structure,
- the technique does not measure the size of single pores,
- if a system of small pores leads to larger pores, the results become misleading because the larger pores will remain unpenetrated until the smaller ones are penetrated. There is insufficient data on peat pores at present to judge whether this is a problem.
- pores smaller than 0.01 μm will not be penetrated.

4.2.2.2 Differential Scanning Microcalorimetry. Differential scanning microcalorimetry (DSC) techniques may be used to determine pore size distribution and porosity of porous materials. Homshaw (1979) has applied DSC to the study of pores in montmorillonite and polyacrylonitrite fabrics.

Water in pores freezes at subzero temperatures. Curves generated by DSC measure the energy associated with water-ice phase transitions in porous materials. If rectangular pore shapes are assumed, Homshaw (1981) has shown that the ratio of lowering of freezing and melting temperatures in pores depends upon the width of the pores. He was also able to take his experiments one step further by introducing salt solutions into samples in order to determine pore length and continuity. The salt solution caused further depression of freezing temperature. Monitoring the spread of the salt solution provided an indication of pore length and continuity.

4.2.2.3 Enthalpy of Fusion. Mraw and O'Rourke (1982) indicated from their work at Exxon Research and Engineering Corporation, that pore size distribution during drying and subsequent rewetting could be determined by calculating the enthalpy of fusion. The enthalpy of fusion of water entering a porous system depends upon the size of the cluster of water molecules involved. The slope of a curve (enthalpy versus water content) reflects fusion of a particular size of water cluster which in turn reflects pore size. Mraw and O'Rourke have used this technique successfully on lignites. They have indicated that the technique has been useful in studying wool, collagen and glass.

4.2.2.4 Adsorption Isotherms. Pore size distribution of small pores (less than 0.1 μm) can be determined from interpretation of adsorption desorption isotherms. They relate moisture content to relative humidity or relative vapor pressure at a constant temperature. Adsorption isotherms are also useful in interpreting water-holding mechanisms in force in a sample. Many interpretation techniques have been developed. Section 7.2.1 describes a curve interpretation technique that has been applied to lignite studies.

4.2.3 Pore Configuration Models

Two types of pore configuration models are in common use for explaining capillary phenomena or macroscopic flow. The first involves visualization of pores or "channels" as spaces between idealized particles. The particles in the simplest models are spherical and uniformly sized. The second involves visualization of various arrangements of capillary tubes. A Canadian researcher, F.A.L. Dullien, Chemical Engineering Department, Waterloo University, has done extensive work on modelling of pore space (Dullien, 1979). His work is being applied in fine coal dewatering studies in the Chemical Engineering Department at the University of Pittsburgh where G. Klinzing's graduate students are currently developing and testing computer models to explain empirical results of their pore studies.

4.2.3.1 Packing Models. In packing models, several particles surround a void space. Neighboring voids are separated from each other by necks. Packing arrangements can be varied to fit the phenomenon being modelled. Particle size and shape can also be varied in order to obtain the porosity of the peat samples that are being simulated.

4.2.3.2 Capillary Tube Bundles. Pore systems can be idealized as a collection of capillary bundles. Each tube in the bundle is the same length and has the same diameter. For preliminary understanding of peat-water relationships, this model is simple to understand and to use. Determination of pore size distribution by intrusion of a non-wetting fluid is based upon this model. The work done by Kandebo (1982) on peat water holding mechanisms used this model.

4.2.3.3 Network Models. Network models present a more complex view of pore systems. They assume that pores can interconnect rather than operate as independent channels. They have irregular geometry. The models can be one, two or three dimensional, depending upon the purpose of the model (Dullien, 1979). An appropriate network model for peats can be chosen only after comprehensive data on pore size and pore size distribution has been gathered. The modeller can vary the configuration of the pore network until it "predicts" the test behavior. It is likely that several different models will produce data comparable to the tests. Further laboratory experiments can then be devised to test the appropriateness of the assumptions made in each feasible model.

4.3 Flow Through Porous Media

4.3.1 Basic Theory

In peats, as in other soils, flow of water, gases, heat and ions occurs simultaneously. It is possible to develop equations to portray the combined flows of water, gases, heat and ions; alternatively, it is possible to study the flow of water separately. Very little detailed microscopic study has been carried out to date on flow of water or any other fluid through peat. Because of the lack of previous study and research, it appears that the most productive research in this aspect of peat study is to examine each type of flow separately, rather than trying to investigate combined fluid flow.

Analyses of fluid flow through porous media are usually based upon a law developed by Darcy in 1856, when he was investigating flow through sands. Darcy's law states that flow rate or flow velocity is directly proportional to hydraulic gradient. This relationship is analogous to Fourier's law for heat flow, Ohm's law for electric current and Fick's law for ionic movement; each of these laws represent numerical values applicable to flow.

When considering the flow of water through peat, it is possible to obtain permeability values in the laboratory or field under controlled flow conditions. There is, however, a major problem in interpreting the results. Changes in soil fabric due to handling of samples in the laboratory or application of pressure during field testing can change permeability by several orders of magnitude. Use of permeability data in flow models must reflect this uncertainty.

In peat dewatering studies, an understanding of heat flow during the drying process is of prime interest. Research relevant to this requirement is described in Section 9.0 on drying measurement and modelling.

Ionic flow rates can be measured under controlled conditions. Researchers concerned with migration of contaminants in groundwater have obtained empirical results and developed computer models to explain the behavior they observed. Peat researchers at the University of Wisconsin and the University of Michigan have studied migration and utilization of nutrients and metal ions in peat deposits.

Use of principles of irreversible dynamics would allow combined flows to be analyzed using one overall coefficient and one flow gradient to describe flow conditions in a soil. Tests aimed at accomplishing this objective on clays have produced inconclusive results (Mitchell, 1976). These procedures are not well enough established to be applied to peat dewatering research at this time.

4.3.2 Flow Models

This section describes single phase flow modelling techniques that may be applicable in describing the flow of liquids and gases in peat. Modellers have used both packing and conduit methods.

4.3.2.1 Phenomenological Flow Models. Phenomenological flow models are commonly used to describe flow in fibrous or granular materials. They relate transport coefficients to grain or fibre properties or packing arrangement. Models of this type have been used since about 1900. The transport coefficients are a function of porosity, particle or fibre size and shape (Dullien, 1979). Determination of these coefficients is time-consuming even for beds of sand. In the case of peat, porosity and "particle" shape changes when samples are handled or external pressure is applied.

Fibrous bed modelling is the most appropriate phenomenological model for peats. It is particularly useful for high porosity materials. Most of the empirical data gathered to-date has been obtained from the flow of gases through fibrous beds. The modelling technique assumes that fluid is not moving in all of the pore space. In some pores, the fluid is present but stationary. The model utilizes an "effective porosity" (volume of flow region/total sample volume). Hydraulic gradient across the bed is affected by viscous losses, drag due to fibre shape and fibre deflection. Empirical data have been obtained on glass, Dacron and Nylon fibres (Dullien, 1979).

4.3.2.2 Conduit Flow Models. Conduit flow models in porous media are roughly analogous to hydraulic models for flow in channels. Two types of conduit models have been developed for porous media: geometrical permeability models, and statistical permeability models.

Geometric permeability models consider flow without consideration of the way in which flow channels may be interconnected. The Carmen-Kozeny theory is used, which assumes that the porous medium can be visualized as a channel with a constant area. Channel diameter is equal to the cross-sectional area of flow divided by the wetted perimeter. Average flow velocity is defined by a Hagen-Poiseulle equation where velocity is a function of flow path length and shape factor. There are variations of this model in use which define effective diameter and shape factors differently but the general principles of modelling are the same (Dullien, 1979).

Statistical permeability models seem more appropriate than do geometric models, because permeability of peat varies so dramatically when the peat is disturbed. Randomly oriented cylindrical pores are used in the model. Each cylinder is described by its length, radius and by two angles that define its orientation in three dimensional space. An average pore velocity is calculated and the resultant permeability is calculated (Dullien, 1979).

4.3.3 Flow of Gases and Diffusion

As indicated in Section 4.3.1, flow of gases in porous media can be described by equations that are similar to those for liquid flow. In modelling gas flow, a few modifications are made. The first relates to flow velocity. In idealizing liquid flow, the velocity at a capillary or conduit wall is assumed to be zero. In gas flow, this assumption is valid only if the mean free path of the gas molecules is less than the pore size. In the large pores in peat, no modification would be necessary. In the smaller pores, this effect would require further study. Diffusive flow occurs when the mean free path of the gas molecules is greater than the pore sizes. In such systems, models for both viscous and diffusive flow are required (Dullien, 1979).

Gas flow through porous media is further complicated by the tendency of gases to adsorb on pore surfaces. Thick adsorption layers can be modelled by assuming the presence of a stationary layer of an appropriate thickness (Dullien, 1979).

4.3.4 Conclusions

The techniques described in Section 4.0 for the characterization of pore space are well established procedures that are already being used and adapted for peat and coal research. It is essential that extensive data be collected on pore space in peat in order to determine the role of pore networks in holding and expelling water. Use of pore configuration modelling techniques will allow researchers to investigate the effects of changes in pore structure on water-holding in peat. Use of these modelling techniques will be valuable in fundamental peat dewatering studies; once appropriate models have been developed, fewer laboratory tests will be required in specific research projects. The modeller can quickly and inexpensively determine the effects of pore structure changes that are likely to occur due to sample compression, drying, freezing, etc. Models for flow through porous media will be very useful in predicting and studying the chemicals on peat dewatering. These techniques are currently used in enhanced oil recovery studies where the effectiveness of surfactants is being investigated (Ramirez et al 1980; Ramirez and Riley, 1984). These models can accommodate changes in boundary conditions at pore walls due to changes in viscosity of the pore fluid, and wetting characteristics of the pore walls. All of the modelling techniques presented in Section 4.0 are useful for the development of theories that explain physical and chemical actions. In peat dewatering research, use of models can save time and money by allowing the investigator to quickly assess the implications of a theory at an early stage in the laboratory investigations and can provide direction in the appropriateness of hypotheses and the techniques and procedures used to test those assumptions and parameters.

5.0 PHYSICAL CHEMISTRY: PRINCIPLES, ACTIONS AND CHARACTERIZATION

5.1 Background

Physical chemistry is that discipline which deals with the interpretation of chemical phenomena and properties in terms of the underlying physical processes, and with the development of techniques for their investigation. Recognition of the capabilities within this field of science, and use of its particular investigative techniques, has increased immeasurably in the past decade. Part of this increase is due to the development and subsequent refinement of tools such as the scanning electron microscope, laser beams, and electronic measuring and computing devices. These changes in technology parallel the needs of industry for improved economics. Empirically-derived data has, in industries such as that of pulp and paper manufacture, essentially reached its limit. The techniques and methods of the physical chemist are now being used to define, and then logically develop, an understanding of the underlying processes that make a procedure work -- or that prevent the manufacture of an acceptable end product. Physical chemistry and its principles are used in activities ranging from food processing to oil well drilling, and from sewage disposal to coal preparation. Research methods used to improve the end products of these industries, and the materials consumed in their processes, have included particle characterization, colloidal and surface chemistry, electrical charge studies, measurement of contact angles, and numerous related methods for both organic and inorganic materials. Throughout the course of this study, researchers consistently reiterated the need for accurate materials characterization, without which effective work is impossible. The following sections include discussions of research within the broad area of physical chemistry, which appears pertinent to the subject under consideration, i.e. the removal of water from peat.

5.2 Characterization

Peat, depending upon its degree of decomposition, may consist of particles small enough to be termed "colloidal"; that is, with the smaller faction of the particle mix sized at 0.2 μm. Systems where the particles fall within the colloidal size range react differently than do those systems of greater or lesser sized particles, due to the very high surface to volume ratios of the system. In addition to the size range, other characteristics of the particles are important in understanding, in predicting, and in modelling the behavior of the substance. Characteristics such as particle shape, mass, diameter, porosity, density, and flexibility are of concern in a colloidal substance; they are also important in large-size particle substances. Several techniques exist and can be used in characterizing particles; some specific examples are given here. The parameters of this study are not intended to provide a comprehensive examination of all characterization techniques; rather, the examples provided here are intended to apprise researchers of new methods, of techniques used regularly or specifically in other (non-peat related) disciplines, or that active researchers have personally indicated as being useful or promising for the purposes of peat characterization. A detailed discussion of current fine particle characterization techniques may be found in a recent publication by Kaye (1981).

Giddings et al (1983) used sedimentation field-flow fractionation (FFF) to characterize effective mass, actual mass, density, polydispersity, diffusivity, and various particle dimensions. In this technique, sedimentation is coupled with the transport effects of laminar flow. Small samples of the material are injected at the FFF channel inlet, sorted by the interplay between field and flow, and are monitored at the exit for refractive index, light absorption, light scattering, viscosity and density. Giddings used a series of five polystyrene latices for experimental purposes; developed capabilities have been used to measure the molecular weight of viruses, viral density, the diameter of albumin microspheres, and the mean and variance in diameter of liposome density. Giddings has concluded that the FFF method yields accurate size distribution curves for latices.

Particle size distribution has also been studied by Cummins et al (1983), who used a particle by particle light scattering approach. This method is particularly useful where other methods are insufficiently accurate, such as the use of electron microscopy, in studying emulsions, or photon correlation spectroscopy and absolute light scattering in the examination of wide size distributions. General advantages of the FFF technique are listed as:

- the predictable characteristics of the method
- experimental flexibility and redundancy
- use of nearly any suspending medium
- small (<1 mg) sample requirements
- high resolution
- fraction collection for additional characterization

Cummins describes the equipment used (a laser illuminated flow ultramicroscope coupled to a photomultiplier with a feedback mechanism). Polystyrene - latex dispersions were used; aggregation of fluorescent latex was accomplished by adding analytical grade reagent $La(NO_3)_3$. The authors indicate that this characterization method is useful in studying many types of colloidal interactions, including particle growth and dissolution.

Another characterization method that may be useful in studying highly decomposed peats has been developed by Melik and Fogler at the Department of Chemical Engineering, University of Michigan. They apply light scattering to measurements of the turbidity ratio for estimating particle size distributions of nonabsorbing isotropic spheres of the micrometer to submicrometer range (Melik and Fogler, 1983). Their method allows the analysis of particles too small for optical microscopy but too large for quasi-elastic light scattering.

Dr. Bragg, now in the Faculty of Engineering at the University of California at Berkeley, was an early user of x-ray diffraction techniques. Current and recent research by Dr. Bragg and his students has centred on graphites and coal-tar pitch, with emphasis on determining the properties of the materials. The use of graphites in nuclear reactors prompted the current research in materials characterization; the experience gained strongly indicates that similar techniques would be useful in identifying peat components and their internal structure.

5.3 Surface and Interfacial Phenomena

The formation of colloidal material involves either the degradation of bulk matter or the aggregation of small molecules or ions. Peat formation is recognized as a process of plant material degradation; the variables in the degradation process range from that of plant matter to climate, from climate to soil parent material, with groundwater flow as an additional factor. While the range of possible originating characteristics is vast, similarities or comparisons have been (or can be) drawn. For example, the presence of humic and fulvic acids directly affect the dewaterability of the peat material. The questions of particle liquid interaction, particle-particle interactions, liquid-liquid and liquid-air activities are the subject of research in fields as diverse as food science and coal technology, biomedical studies and tar sands extraction, papermaking and secondary petroleum recovery.

Research conducted for these and other fields may well be relevant to improvements in the end use of fuel peats.

5.3.1 Interfacial Tensions

Donald F. Gerson, Director of the BioTechnology Division at the Alberta Research Council, has done extensive work in the determination of interfacial tensions by measuring the contact angles. Gerson and his associates (Schurch, Samuel, Gerson, McIver, 1981) used aqueous two-phase systems of dextion and polyethylene glycol in their studies of cell/medium interfacial tensions. Determination of the limiting or critical interfacial tension may be a useful tool in studying cell surface properties such as hydrophobicity or adhesion.

Researchers at the Department of Chemistry, McGill University, in affiliation with the Pulp and Paper Research Institute of Canada, have conducted substantial investigation into the measurement of contact angles, and the related wetting and spreading parameters as related to pulp and paper (Oliver and Mason, 1976, 1977). The manner in which a liquid wets and spreads on the surface and into the substrate of paper is important to the processing and use of that material. Factors affecting the angle of contact between paper and liquid include sheet roughness and porosity; sharp edges are especially inhibiting to liquid spreadability.

Valuable insights to the effect of surface roughness were produced by these studies for which scanning electron microscopy was used.

Direct force measurements between molecularly smooth mica surfaces in liquids were reviewed by J.M. Israelachvili (1982). The review included the current understanding of the four fundamental particle liquid interactions: double layer, van der Waal's, structural (solvation) and adhesion forces, and a comparison of the experimental measurements and theoretical concepts applicable to those forces.

Further discussion of the forces operating between particles and their liquid mediums was undertaken by Ninham (1982), who advocates a re-examination of Poisson's theories to elucidate small distance forces.

The high cellulosic content of peat, and the documented and theoretical presence of bound water, may have relevancy to work conducted by C. Ballario and associates (1980). Their study investigated the microwave dielectric-properties of colloidal aqueous polystyrene suspensions as related to temperature and ionic strength. The study materials consisted of powdered cellulose mixed with deionized water. Measurements confirmed that liquid water was present, below the freezing temperature of normal water. This liquid water exhibited different dielectric properties than those of bulk water, and is termed "modified water" by the project investigators.

5.3.2 Sorption Phenomena

Sorption phenomena play a major role in particle-liquid interactions; the phenomena affect a wide range of materials and processes, from fertilizer uptake to oil recovery. The adsorption capacity of peat has long been recognized, it is particularly useful in the treatment of wastes. McKay et al (1981) noted that peat has been used as an adsorbent in oil spill cleanup, as a mechanism for removal of phosphates in sewage waste, as a water purifier for slaughterhouse wastes, and as a medium for metal ion exchange in effluent streams. The aim of the McKay et al study, conducted at Belfast's Queen's University, Department of Industrial Chemistry, was to determine the parameters that affect the surface mass transfer of Astrazone Blue dye on peat. Removal of dyes and pigments from textile industry wastewater is a major problem; the low cost, ease of availability, and high adsorption capacities of peat made it an ideal substance for this purpose. High adsorption levels were obtained due in turn, to the strong cationic exchange between the dye ions and the acidic hydrogens in the carboxylic and phenolic hydroxyl groups, due to the presence of humic and fulvic acids (McKay, 1981). The cationic exchange is a complex mechanism, and is due to chemisorption and physical adsorption on lignin and cellulose components. The researchers were able to prepare a limited model of the transport processes; limitations were due to the complexity of the dye solution and peat particles, and the difficulty in assigning a representative specific surface since peat particles are not true homogeneous spheres.

The adsorptive capacities of wetlands has resulted in their use as sewage treatment systems, with substantial renewed interest and design work in the past decade. The U.S. Environmental Protection Agency funded a research project by Hammer and Kadlec of the Department of Chemical Engineering, University of Michigan, from which a comprehensive report was issued (Hammer and Kadlec, 1983). Adsorption of phosphorus and ammonia are major constituents of an effective wetlands wastewater system. Distribution of phosphorus and nitrogen nutrients in the Houghton Lake, Michigan, wetland system were further documented by Hammer and Kadlec (n.d.) in a report on the system's operation over a 6-year period. Further work by Kadlec and Rathburn (1983) indicates that peat is an excellent sorption medium for copper, particularly if pH is low. Similarly, where a pH value of 2.0 exists, the resulting low ionization of 2,4-D in aqueous solution favors its adsorption on peat surfaces (Clouthier, LeDuy and Ramatho, 1985).

5.3.3 Surfactants

Related to the sorption phenomena is the action of surfactants, substances used to alter surface tensions. Addition of other substances to the surfactant itself may produce drastically different results than those obtained through use of the surfactant alone.

Ramirez and Riley (1984) investigated the changes in mass dispersion and permeability caused by surface active agents, and showed that surfactant adsorption to rough surfaces such as those of the Berea sandstone increases interfacial momentum transfer. The dispersion increase and permeability reduction is caused by a highly viscous film near the solid surface, with resulting changes in fluid viscosities which in turn produce velocity pore profile exaggerations. The study was conducted with a non-ionic surfactant (Triton X-100), using sucrose as the tracer, and Berea sandstone cores as the porous media. The study results will be used in the design and interpretation of systems in enhanced oil recovery processes.

Berea sandstone was also used as the porous medium for research conducted by Krumrine et al (1980) in determining the effect of alkaline additives on interfacial tensions, specifically applied to surfactant adsorption and the resulting efficiency of enhanced oil recovery in low-tension waterfloods.

Krumrine's study objective was to test the effectiveness in the use of sodium silicates as additives for dilute surfactant systems. He used two light crude oils, synthetic brines, Petrosep petroleum sulfonate surfactants, and sodium silicates. Conclusions were that alkaline chemical additives improved residual oil recovery; surfactant adsorption or retention can be reduced by sodium silicate, sodium tripolyphosphate and sodium carbonate; harmful ion levels are reduced by alkaline chemicals; and that minimum interfacial tensions of Illinois crude oil can be obtained with high pH values.

Biological surfactants have also been used in the petroleum industry to improve recovery both from in situ wells and from extracted tarsand. Biosurfactants from peat are discussed in Section 3.0. David G. Cooper of the Department of Chemical Engineering, McGill University, has done extensive research into the use of surfactants in the petroleum industry, including their use in tarsands, enhanced oil recovery, and demulsification. Cooper (1983) reported the production of an economically feasible biosurfactant from Torulopsis bombicola yeasts, for use in a cold-water tar sands extraction process. The process for which the surfactant was developed was terminated with the sudden economic downturn of the early 1980's; production of the surfactant also ceased.

5.3.4 Flocculation

Flocculation is a process by which small particles join together, facilitating their separation from an aqueous medium. The process is most frequently used in sewage treatment, and in the treatment of tailings (mine wastes). Narkis and Rebhun (1975), from the Israel Institute of Technology, have studied and reported on the processes of flocculation in systems where humic substance content is high, as it is in peat bogs. They found that the salts of humic and fulvic acids (anionic polyelectrolytes) react chemically with the polycationic flocculant through carboxylate and phenolate groups. Cationic polyelectrolytes added to clay or organo-clay complexes react first with free organic acids; only after complete reaction with the humates and fulvates does flocculation begin. In a later study (Narkis and Rebhun, 1977), the same researchers concluded that the degree of ionization is dependent upon the pH value of the suspension, and that there is a stoichiometric relationship between the concentration of the anionic groups and the flocculant demand. At a low pH, there is a decrease in the degree of organic molecule disassociation, with a corresponding reduction in flocculant demand. These two studies were conducted with model systems and reference clay. They recently reported on their findings of the effect of organics in a naturally-occurring situation - that of a playa lake in Texas (Speber, Narkis and Rebhun, 1984). Results of their study with naturally-occurring materials confirmed their previous hypothesis that the humic substances present in turbid surface waters are the major factor in determining flocculation behavior.

5.3.5 Emulsions

A further type of colloidal dispersion system is an emulsion, a combination of two phases that cannot be mixed (i.e. oil and water). There are two basic types (O/W and W/O) of emulsions; a more complex substance is the water-in-oil-in-water multiple emulsion. These substance types have become more important recently due to their use in hydrocarbon separation, treatment of wastewater, immobilization of enzymes, prolongation of drug release, and treatment of drug overdosage. Florence and Whitehall (1981), at Glasgow's University of Strathclyde, have made an attempt to define and record the critical features of breakdown in different W/O/W emulsions, stabilized by nonionic surfactants. The research methodology included photomicrography and cinemicrography with which droplet coalescence was photographed. The researchers indicated that observations and calculations strongly suggest that water transport through the oil layer is by way of inverse micellar species.

Examination by electron microscopy of the liquid phase of a substance, or materials containing O/W or W/O emulsions, is precluded by the necessity for a vacuum in the microscope's observation chamber. To resolve this problem, the freeze-fracture technique has been developed, and has been used by James E.

Zajic et al (1981) to examine consolidated lumps of bituminous sand. The study objective was the examination of the physical relation of sand, clay, and bitumen. The study observations indicate that the bitumen in bituminous sand is, in fact, present as a water-in-oil emulsion with the bitumen in the continuous phase. The freeze-fracture examination technique indicates that there is not a layer of water surrounding each sand or clay particle, as has previously been believed.

The multivariate science of colloids, first identified just over a century ago, has direct application to the subject of this study. Characterization of the material, followed by the application of principles utilized by the scientists for other media, will help to produce the data required for more effective use of peat resources.

6.0 CELLULOSE - LIGNIN DEGRADATION

The composition of peat naturally reflects the composition of the materials from which it was formed, and the subsequent processes that took place. Cellulose comprises a large portion (15 percent) of the original plant carbohydrate fraction; it forms the cell walls and gives woody plants their characteristic shape. As peat decomposes, the carbohydrates are converted to sugars; this process takes place more readily in low-moor than in high-moor peats. The cellulosic cell walls are cemented together by lignin, a high molecular weight, stable material. Lignins occur primarily in strongly fibrous plants: trees and shrubs, grasses, reeds and sedges. The mosses and liverworts do not contain cementitious lignins.

The importance of lignins and celluloses in this study relate to the function of those substances in utilization of peat as a fuel, and in particular, to the water-holding capacity of the cellulosic cells. As has been previously indicated in this report (Section 2.2), water is retained in the pore networks within the fibrous structure and within the cells of the plant material. Removal of this water depends upon the rupture of cell walls through extreme pressure (Wilson, 1978), or by degradation of the cell wall structure. Processes that have been developed to degrade cell wall structure, enabling release of or access to cellulose, include acid hydrolysis, liquid/heat treatment, and microbial action. Combinations of these processes may be sequentially used, to take full advantage of the characteristics and benefits offered by each method. These steps may be used as pretreatments of biomass for use as fuel, may be a means of converting cellulose to digestible feed material, or may be applied to a number of problem areas in the pulp and paper industry (Kirk, Tien and Faison, 1983). As previously indicated, the intent of this section is not to provide an extensive documentation of current biomass fuel technologies, but to provide an update of research that is more directly relevant to the subject under consideration.

6.1 Pretreatment Procedures

The economics relevant to fuel use of biomass as compared with conventional fuels dictate that biomass pretreatments must:

- use inexpensive chemicals and require simple equipment and procedures
- solubilize the lignin and hemicellulose
- reduce the crystallinity and thereby enhance the hydrolysis of the cellulose to D-glucose
- be suitable for pretreating a wide variety of plant species (McGinnis, Wilson, and Mullen, 1983).

A comparison of four pretreatments of woody biomass (autohydrolysis, wet oxidation, steam explosion and rapid steam hydrolysis) was presented by Schultz, McGinnis and Biermann (1983), who indicate that these and other older processes are being re-examined with new technologies.

Autohydrolysis results in considerable degradation of hardwood lignins. The process treats wood with water at temperatures of $185^{\circ}C$, causing the formation of organic acids; solubilized hydrocarbons form furfural which in turn may react with lignin to form a copolymer. Autohydrolysis appears to be most effective with aspen.

Wet oxidation treatment substantially increases the rate of acid hydrolysis of the cellulose faction of woody biomass. Initial wet oxidation work, conducted by Schalenger and Brink and the University of California (Brink, Faltico and Thomas, 1976), indicated that the initial reaction during wet oxidation is the formation of acids. Brink indicated, during discussions at the university of California's Richmond Forest Laboratory, that his work is continuing, and is now centred on hydrolysis. He also indicated that treatment of biomass (particularly peat) with hydrogen peroxide as an oxidizing agent is an area that could be useful. That statement correlates well with the work of Kirk and Gold (see Section 6.0).

Steam explosion is a process first developed by Mason in the mid-1920's as a method to utilize wood chips as hardboard components. The process results in lignin breakdown, hemicellulose breakdown, and an increase in the accessibility of cellulose to enzymatic hydrolysis. Steam explosion has also been used on rice hulls, corn stalks, and sugar cane bagasse (Schultz et al, 1984). Researchers subjected the biomass materials to a range of temperatures (192^{o}C to 252^{o}C); NaOH, H_2SO_4, and $Fe_2(SO_4)_3$ were used as catalysts; materials were steam exploded for one minute. Results of the research indicated that steam explosion pretreatment resulted in degradation of over 90 percent of the hemicellulosis, and that a portion of the lignin will not be solubilized in hot aqueous alkali, while up to 50 percent of the cellulose will be solubilized.

Rapid steam hydrolysis/continuous extraction is a process similar to steam explosion, except that the soluble or gaseous products are continuously removed from the reaction zone. The process uses high temperatures, which cause hydrolytic depolymerization of the hemicelluloses and lignin; catalysts are not used. In this process, up to 95 percent of the lignin is extracted by aqueous alkali or organic solvents; the addition of selected catalysts or reagents allows selectivity in extracting or altering the lignin or polysaccharide components.

6.2 Cellulose as a Dietary Nutrient

The impetus for developing single-cell protein (SCP) from cellulose arises from the need (and associated expense) to dispose of wastes from the pulp industry. In Canada alone, disposal of the greater than 400 000 tonnes of waste requires an annual expenditure of $8 million (Tautorus and Chalmers, 1984). A Canadian company, Envirocon Ltd., opened a pilot plant in Vancouver in 1982, from which is produced two tonnes per day of SCP. The process, developed by Murray Moo-Young at Waterloo University, uses a fungus (*Chaetomium cellulolyticum*) to break down the otherwise largely indigestible lignocellulose fibres. The process can also utilize raw substrates that are readily available as waste by-products: sawdust, straw, corn stover, bagasse, coffee grounds, animal manures, and canning industry wastes. The system uses a low-technology process that begins with a sludge (20 percent w/v solids), that is first cleaned and sterilized, and then fermented. The product is transferred to a production fermenter, then recovered, washed in a vacuum-drum filter, and dried in a rotary drum drier.

Single-cell protein has also been produced from a peat hydrolyzate, under a process developed by A. LeDuy at the Department of Chemical Engineering, Laval University (LeDuy, 1979). LeDuy's method requires acid hydrolysis of relatively undecomposed peat; the process is, therefore, of interest but only of tertiary relevance to this study.

Researchers in the Chemistry Research Division of the Philippine Atomic Energy Commission in Quezon City monitored the growth of *Myrothecium verrucaria*, a cellulolytic micro-organism, on irradiated and non-irradiated cellulosic material. They found (Dela Rosa, 1983) that irradiation with either gamma rays or electrons resulted in degradation of cellulose. These researchers used agricultural and cellulosic wastes; they briefly discussed the findings of other researchers regarding the effect of irradiation on cellulose. Data presented indicated that radiation pretreatment significantly affects the structure of cellulose, resulting in an increased yield of reducing sugar.

6.3 Lignin Oxidation by *Phanerochaete chrysosporium*

Lignin degradation for the purpose of cellulose release or accessibility as in peat dewatering has likely received substantially less attention than has its application in the pulp and paper industry. Potential uses of lignin degrading systems in that industrial sector have been examined in the past decade; research has been accelerated to develop applications in wood pulping, bleaching, fibre surface modification, wastewater cleanup, and conversion of lignins to useful chemicals (Kirk, Tien and Faison, 1983).

Working independently, both Kirk (USDA Forest Products Laboratory, Madison, Wisconsin), and Michael H. Gold (Department of Chemical, Biological, and Environmental Sciences, Oregon Graduate Centre, Beaverton, Oregon) have isolated and characterized a lignin-degrading enzyme from the basidiomycete *Phanerochaete chrysosporium*. The basidiomycetes are a class of fungi responsible for numerous plant diseases; in this case, a white rot wood decay.

Kirk's presentation of his findings to a symposium on Biotechnology in the Pulp and Paper Industry (1983), included a description of his work and proof of the lignin-degrading enzyme. The enzyme is responsible for catalyzing the C-C cleavage reaction, known to be important in lignin degradation. Kirk indicated that other reactions are also important in the lignin degradation process: methoxyl demethylation, aromatic hydroxylation and ring cleavage. Gold et al (1984) also indicates that the isolated white-rot fungus enzyme requires hydrogen peroxide (H_2O_2). Gold and his associates purified by the H_2O_2-requiring oxygenase ion-exchange chromatography and gel filtration.

Researchers under Pierre Chartrand at the Department of Microbiology, University of Sherbrooke, Quebec, are working on the identification and isolation from white-rot fungi genes, the code for lignin-modifying enzymes (Chartrand, 1984). The researchers have screened 50 000 representatives with cDNA probes for lignin-modifying activity; the ultimate intent is the mass production of the enzymes, to facilitate lignin modification.

6.4 Conclusions

These studies, while of direct benefit to the pulp and paper industry, may well have indirect benefits for the peat industry, considering the relationships between the primary materials used. Fundamental understanding of basic dewatering mechanisms in biological materials may be appreciably clarified through study not only of fluid flow processes, but also through the study of biological process reversals. The factors and parameters of plant structure degradation may provide researchers with greater insight into the role played by each plant component, including individual and synergistic component effects on water retention.

7.0 RESEARCH ON WATER-BINDING MECHANISMS

7.1 Introduction

The desire to understand the mechanism of water-holding is not confined to peat research. Similar inquiry is under way in the food industry, in agricultural engineering with respect to animal and botanical wastes, in mining engineering with respect to low rank coals, and in municipal engineering with respect to sewage. In all cases, there has been a need to identify the dominant water-holding mechanisms and to assess their relative importance.

This section describes the work being undertaken in these fields, and which may be relevant to the peat dewatering problem. A brief survey of the investigative procedures being used is included.

7.2 Research Status in Selected Fields

7.2.1 Coal Studies

Lignites can have moisture contents of 30 to 70 percent. D.J. Allardice completed a Ph.D. thesis on The Water in Brown Coal in the Department of Chemical Engineering at the University of Melbourne in 1968; he and D.G. Evans have continued to publish papers on this topic, and in 1978 published a state-of-the-art review (q.v.) on the topic. It is useful to quote from this work:

> "Terms of describing the bonding of water in coal, such as free, bulk, surface, capillary, inherent, colloidal hygroscopic, combined, bound, adsorbed and even dissolved water have been used with little attempt at rigorous definition."

Research undertaken by Allardice and Evans on water-holding mechanisms involved measuring water sorption isotherms at 30°C. Moisture content as a function of relative humidity was determined using a vacuum micro-balance technique. Isotherms (moisture content versus relative humidity) were interpreted as follows:

- Water removed at vapor pressures close to the saturation pressure was designated as free water. This represented the asymptotic section of the desorption curve (42 to 67 percent moisture content).
- The concave portion of the curve represented water from capillaries (15 to 42 percent moisture content).
- The convex portion of the curve was attributed to hydrogen bonding. At moisture contents of 7.5 to 15 percent water was said to be weakly hydrogen bonded to a layer of water on the coal surface.
- Water remaining in a sample when the moisture content was below 7.5 percent was designated as water that was hydrogen bonded to organic groups within the coal.

Agroskin, Lyashchenko and Svyatets (1979), summarized Russian research on chemically bound water in brown coals. Previous studies on the sorption capacity of coal showed that drying at 100°C did not drive off all the water. A small amount of water remained until the samples were heated to 400°C; this water was termed "strongly adsorbed water". The authors' investigated this phenomenon further by heating samples to 365°C after they had been dried at 105 to 110°C. The samples had to be heated above 125°C before further water was liberated. They concluded that water held in coal above 125°C was chemically bound.

Further study of the binding mechanism(s) involved an investigation of whether the water was bound to the organic or inorganic constituents of the coal. From tests on coals of varying ash contents, they concluded that most of the water was bound to the organic matter. This conclusion was also supported by tests that indicated that organic groups in the coal decomposed at a temperature of about 245°C.

Agroskin, Lyashchenko and Svyatets (1979) identified OH^-, $COOH^-$ and CO^{-2} groups within the organic fraction as the active "formers" of hydrogen bonds with water. The investigators recommend further study of the behavior of humic acids when subjected to heat to obtain more detailed information on the hydrogen bonding configurations. Humic acids should liberate water and carbon dioxide as their structure is disturbed by heating. The investigators found that some disruption occurs at temperatures as low as 100°C.

Dr. Harold Bale, University of North Dakota, Physics Department, is currently investigating and developing methods to determine pore size distribution in coals by small angle x-ray scattering. He is attempting to monitor changes that occur during heating, drying and pyrolysis and to relate these changes to release and gain of moisture. His findings will be applied to coal processing technology.

The University of North Dakota, Energy Research Center, is conducting a study on physical properties and moisture in low rank coals. The aim is to determine the distribution and modes of incorporation of water in low rank coals and to develop procedures to measure the amount of moisture held in each mode. They have investigated the effect of temperature on diffusion of adsorbate into fine pores. They found that a rise in temperature increased diffusion into narrow pores.

Investigators at the University of North Dakota have determined heat of wetting values for lignite samples. Their purpose in these tests is to indirectly determine the surface area of the samples. A differential calorimeter was used in these tests. Further work on this project will allow researchers to investigate pore size distribution by using wetting liquids of differing molecular sizes.

At the University of North Dakota, dielectric relaxation studies have been conducted on lignite samples using a precision capacitance measuring system. When the samples are subjected to an electrical current, charges within the lignite - water system tend to rotate, aligning themselves with the electric field. In the vicinity of large pores within the lignite sample, maximum rotation (relaxation) occurs. Where water is tightly bound, little relaxation is observed. The researchers hope to test peat samples in the near futuere (U.S. D.O.E. Quarterly Reports).

Studies on adsorption phenomena in coals and the effect of surfactants on coal slurries is underway at CANMET in Edmonton. Complementary work has been conducted by Dr. J. Kwak, Department of Chemistry, Dalhousie University.

At the University of West Virginia, Dr. H.V. Fairbanks and his colleagues have studied the behavior of fine particles (particularly coal) in ultrasound assisted dewatering and filtration. Use of ultrasound in drying increased the drying rate and lengthened the time that the constant drying rate applied. The investigators found that ultrasound increased air turbulence at the coal surface and the evaporation rate. The constant rate drying period increased because ultrasound decreased the friction factor in the pore "flow channels" of the coal, thereby allowing water to move more easily to the surface (Otsuka and Fairbanks, 1977).

In slurry filtration studies (Fairbanks, 1973) where ultrasound was used, it became apparent that its effect was similar to that observed from studies of particles in air.

Small particles oscillate with the sound waves and are carried along by the surrounding fluid. Large particles are unaffected. Medium size particles tend to collide with each other which enhances coagulation. In these studies, particles larger than 15 μm were unaffected, coagulation was enhanced between 2 to 15 μm (depending on the fluid properties) and particles smaller than 2 μm were carried by the fluid stream.

7.2.2 Sewage Sludges

The separation of sewage sludge solids from their suspending fluid constitutes a major difficulty. Processes that have been used to resolve the problem include flocculation, microbial activity, and polyelectrolyte additives. It has been suggested that a major factor in sewage sludge water retention is the high proportion of cellulosic materials that occur in the sludge.

C.F. Forster, of the Civil Engineering Department, University of Birmingham (England), has conducted research into the water-holding mechanism of sludges, and the modification of those mechanisms. His most recent work indicates that bound water in sewage sludges is associated with rheological properties of the material (1983). Settlement characteristics of the sludge are also affected by the amount of water bound by surface biopolymers.

Forster (1983) measured the viscosity of the sludge and its bound water concentration to:

a) determine the role of bound water in relation to sludge viscosity

b) ascertain (if possible) the nature of the polymers that bound the water

Bound water measurement was taken by the dilatometer technique, which operates on the assumption that bound water does not freeze, although free water does, when a substance is cooled from 20°C to -20°C. Forster found that proteinaceous material is an important factor in determining the viscosity of activated sludge. Further data indicate that, as the viscosity of the sludge decreased, so did the bound water concentration. His studies did not enable the computing of a mathematical relationship between viscosity and bound water concentration; neither was a relationship defined between the bound water and proteinase-, lipase- or cellulase S-sensitive material. The study did, however, confirm that surface properties of the sludges affect viscosity, and that bound water may determine rheology which can be affected by the presence of heavy metal ions.

7.2.3 Food Products

Water is removed from products primarily by expression (i.e. squeezing or pressing). The water content of foods may be as low as 10 percent w.b. in spent coffee grounds, or as much as 70 percent w.b. for pectin greens. In this latter case, Schwartzberg, Rosenau and Richardson (n.d.) maintain that "water plasticizes the solid and prevents compression-induced fragmentation of the solid." Oil seeds, on the other hand, may contain as little as 1 percent of oil; that amount of oil can be removed by expression from the brittle oilseeds. These researchers indicate that freezing appears to facilitate water removal from gels, and from cellulosic materials. Expression tests were conducted on Delicious apples, polyfoam sponge, coffee grounds, and chopped alfalfa, and a means for investigating the expression process was developed. Characterization and correlation of compaction-induced stress, identification of stress during outflow, and other factors were delineated and correlated apparently for the first time. These factors may be correlated with the processes that take place as free water expression is completed and bound water expression begins.

Previous investigations reported by Schwartzberg indicate that fluid in the particles is only released through cell wall rupture; rupture has been measured by Schwartzberg by using a substance of high molecular weight such as gelatin or dentron blue.

Studies indicated also that fluid viscosities of fruit juices increase as higher percentages of juices are squeezed out, presumably because of the displacement of dilute intercellular juice by stronger intra-cellular juice.

Bound water studies in the food industry in general, indicate a similar lack of definition that is apparent in other industries. Researchers have indicated that their primary concern is stabilization of the food product, and retention of flavor and aroma qualities. The role of bound water in foods has not had widespread identification as being of significant importance to the priorities of the food industry.

7.2.4 Pulp and Paper Studies

The pulp and paper industry is actively sponsoring research in the role of bound water, likely due to the multiplicity of ways in which it may affect the industry's processes, from pulp production to waste disposal.

Substantial research has been undertaken or sponsored by large organizations such as Weyerhaeuser Inc. in Tacoma, Washington, and is discussed in Section 8.0. The most important aspect of bound water in the pulp industry is related to the use and efficiency of waste wood particles as a source of fuel. Up to one-third of the total moisture in biomass is termed "bound water";

the term is generally applied to both physically and chemically bound water. In this, as in other industries, a clear-cut definition of the term is lacking. Researchers interviewed during this project most commonly used the term in reference to water that was physically bound; they did not include chemically bound fluid (i.e. water of hydration) in their definition of the term.

In addition, it appears that the pulp industry is currently expending more time and money on research aimed at moisture removal (or drying) than on theoretical studies of water-holding mechanisms.

7.3 Hydrogen Bonding

Very little is known about the role of hydrogen bonding in water retention in peat. Basic hydrogen bonding studies are being carried out in several countries. Information presented in this section was obtained from analysis of work being carried out at the University of Michigan, Chemical Engineering Department, Hydrogen Bonding Group, Institute of Chemistry; University of Uppsala, Department of Chemistry, University of Montreal, Department of Chemistry; University of Ljubljana and Ford Motor Company.

Infrared spectroscopy is a valuable investigative tool in recognition of the presence of hydrogen bonding and in its characterization (Hadzi and Bratos, 1976). Infrared stretching frequencies are shifted to lower wave numbers (Schuster, 1976). This method of detection is most reliable for weak hydrogen bonds. Integrated infrared intensities increase as the strength of hydrogen bonding increases (Hadzi and Bratos, 1976). If Raman spectroscopy is used, the Raman intensity decreases when hydrogen bonding occurs.

IR bands broaden when hydrogen bonds are present. In water, band widening has been attributed to distortion of water molecules due to collisions with each other (Hadzi and Bratos, 1976).

Long wave length vibrational spectroscopy provides an additional method of detecting the presence of hydrogen bonds. It is regarded as a useful tool in investigating the rate at which hydrogen bonds are formed or broken and in studying the behavior of large organic molecules that contain hydrogen bonds. Research is also ongoing to improve techniques for studying surface adsorption phenomena (Rothschild, 1976).

High resolution nuclear magnetic resonance (NMR) studies have been conducted for about the last 15 years to study hydrogen bonding in liquids. Small energy differences which reflect details of molecular structure and conformation can be detected

(Ryan, 1981). Electron density of the molecules involved in hydrogen bonding decreases and causes NMR signals to shift to lower magnetic fields (Schuster, 1976). At the University of Michigan, Chemical Engineering Department, techniques have been developed to distinguish between hydrogen bonding and water of hydration using NMR.

8.0 DRYING MEASUREMENTS AND MODELLING

The efficient and non-degrative drying of materials is of crucial importance in an entire spectrum of fields, from foods to fuels, and from textiles to paper-making. Substances are dried to:

a) produce a usable material

b) stabilize the product and prevent growth of micro-organisms

c) prevent self-combustion

d) enable economic product transportation

The drying process has been segmented into two definite periods: the constant-rate period, and the falling-rate period.

During the constant-rate period, moisture loss is controlled by the external conditions of air velocity, temperatures, and humidity for direct to convection drying; and by heated surface temperatures, effectiveness of contact between the wet solid and heated surface, and the degree of agitation for indirect drying. The falling-rate period follows the constant-rate drying interval; the internal mechanisms of moisture flow is the controlling factor during this latter period.

In recent years, the mechanism and rate of water removal has taken on greater significance than was previously the case, primarily because of the rise in energy costs and the resultant necessary economics in all industrial sectors. Basic research has included the acquisition and collection of primary data. New measuring techniques and parameters have been developed; microprocessors and computers have been used to facilitate the measuring and subsequent modelling processes. Current technology enables researchers to acquire and manipulate data more accurately than was formerly possible. Reviews of published literature and personal discussions with researchers indicate recent substantial advances in our knowledge of drying mechanisms. The intensity of the recent surge of interest in drying, together with the multiplicity of disciplines researching the subject, appears to have been conducive to the application of differing terms to a particular process. Care in precisely defining terms is necessary.

8.1 Stabilization Drying

8.1.1 Food Industry

The food industry's primary interest in drying is to stabilize food products, thereby preventing the growth of micro-organisms. The industry must, however, work within rather restrictive parameters; the end products must not only be stabilized, but must retain high standards of nutritional value, flavor and aroma. Food scientists have adopted or adapted a variety of processing methods to their use, including spray drying, fluidized bed drying, vacuum band drying, drum drying, and freeze drying. Both free and bound water affect the quality and preservation characteristics of food products; the opposite problems of solubility and rewetting are also of importance, particularly in the dairy product portion of the industry. Research on food drying is being carried out in both the universities under the food science and household economics faculties, and in corporate organizations such as Borden, Inc. That company, which began operation with a vacuum pan milk condensing operation over 125 years ago, maintains a research facility that runs product drying test procedures as part of its corporate mandate. The type of drier used depends upon the product to be dried; for example, the new vacuum band drier is used for hygroscopic and heat sensitive products such as citrus juice products. Powdered skim milk is produced by the spray drying process; sweetened condensed milk contains too much sugar to be dried by that method, but could be suited for vacuum band drying.

The models developed to depict and predict the drying of foodstuffs use the principles that are applied to all other biological materials. Fortes and Oakes (Advances in Drying, 1980) state that:

> "Data for biological materials are sparse, rare, and frequently incomplete in terms of drying analysis, and greater efforts should be made in this area."

8.1.2 Freeze Drying

Freeze drying is the most expensive form of drying, but produces the highest quality product. It is used primarily for materials that are heat sensitive, such as pharmaceuticals, foodstuffs and biochemical products. The freeze drying process enables rewetting, or rehydration, because the process does not cause collapse of the cell structure. The high cost of freeze drying is due to energy costs during the long drying time, and to the use of vacuum. Accurate prediction of drying time termination can substantially affect energy costs: a sorption-sublimation model has been developed to facilitate that prediction (Hillman, Liapis, and Marchello, 1984). The study also developed bound water profiles, which will be useful in quality control for freeze drying. Skim milk was used as the subject material in the research project.

8.1.3 Textile Industry

Drying is considered the most important step in the textile processing industry; as the final step in finishing, an error in drying could be disastrous economically. Too little moisture removed could result in mildew growth during storage; excess drying causes thermal degradation resulting in fibre brittleness or scorching. Ideally, textiles should be dried only to the point where the fabric moisture contact equals the amount of moisture it would acquire during storage.

No suitable measuring device has yet been developed to successfully correlate fabric drying and reabsorption characteristics with air temperature and humidity, and with dryer control.

Textile drying detectors are based on a closed water-and-fibre system or on the actual fabric temperature, which is a function of the fabric moisture content. All automatic controls regulate the internal conditions of the tenter (drying machine). Dr. K. Slater of the Textile Science Division, University of Guelph, has done extensive research into the processes of measurement of textile drying.

Textiles exhibit the same constant-rate and falling-rate drying phenomena as do other materials; the transition occurs at what is termed the critical moisture content. A special relationship exists between the moisture content of a fabric and of the air via equilibrium contact with it ("A new technique . . .", 1976). Development of a control system not affected by moisture-laden air from early drying stages could facilitate the use of exhaust air for monitoring purposes; economics in energy use are the ultimate goal.

The award-winning paper of the Ontario Section, Canadian Association of Textile Colorists and Chemists, entitled "A new technique for measuring the moisture content of fabrics during the drying process" (1976) details the procedures used to measure fabric temperature and moisture, and humidity and temperature of the air, for the purpose of identifying a regain value constant for all fabrics, and the resultant possibility of electronically controlling tenter drying. The researchers were successful in developing the relationships among textile variables so that, given the fabric weight, a single equation that holds true for all fibre contents and drying conditions may be used in the design of control equipment.

8.2 Agricultural Products

8.2.1 Grain Drying

The drying of agricultural products, from corn to soybeans to cereal grains, has become a standard part of agricultural operations in the past two decades. The cost of drying these products is disproportionate to the total production cost; Keener (1981) indicates that drying may require 35 percent of total crop production energy cost. Increased dryer efficiency is necessary; improved understanding of the drying process is a pre-requisite to redesign of dryer systems. A substantial amount of research has been completed and reported on by the American Society of Agricultural Engineers. Kumar, Blaisdell and Kerum (1982) developed a mathematical model for moisture diffusion in a composite cylindrical body (ear corn); Sharaf-Eldeen, Blaisdell, and Hamdy (1980) published their model for drying of ear-corn in 1980, with which they were able to predict the drying behavior to within less than 1.0 percent moisture content. Sabbah et al (1979) reported that use of the reversed-direction air flow (RDAF) drying method resulted in better seed quality and more uniform drying than was usual in other deep-bed drying methods. A computer simulation study of energy-efficiency and drying uniformity in RDAF was developed. Comparisons were drawn between reversal and conventional drying, air flow rate effect on RDAF and one-directional air flow (ODAF), temperature effects, and initial moisture effects. The researchers concluded that RDAF drying gave more consistent results, and that lower drying temperatures and higher humidities were significantly better with the RDAF method.

8.2.2 Biomass Waste Drying

Biomass disposal is a major concern in those parts of the world that produce crops with large amounts of waste residues. For example, the state of California alone has approximately 5 000 000 ha of orchards and vineyards, all of which must be pruned regularly. In addition, disposal of corn stover and rice straw is a major problem; given optimal conditions, however, these materials could be used as fuel sources. The most crucial aspect relevant to fuel use is the moisture content: rice straw may have 65 to 85 percent moisture (w.b.) at harvest time; corn stover may contain 65 percent water; and tree and grape prunings may hold 30 to 50 percent moisture, as they are still living at the time of harvest. To avoid self-combustion in storage, the moisture content of these materials must be reduced to less than 20 percent (w.b.); in California, natural field-drying is common. Predicting the optimal time for gathering the biomass wastes for storage or use is dependent upon the extrapolation of moisture content data.

Jenkins, Ebeling, and Rumsey (1984) of the Department of Agricultural Engineering, University of California at Davis described their approach to the question of drying modelling and presented a model for the simulation of field drying. They used the energy balance approach, recognizing that the major problems are those of rewetting by rain, dew, or soil moisture. Rewetting of rice straw, for example, slows the drying process substantially due to cell shrinkage; after the fist rewetting/drying cycle, no further slowing occurs.

In January of 1985, Jenkins and Ebeling described the system they had developed for measuring the natural drying rate of biomass. They used standard equipment (with some modifications) to monitor:

- insolation
- air temperature
- air relative humidity
- wind speed
- wind direction
- dew formation
- precipitation
- soil moisture
- surface temperature
- air temperature under tray
- air relative humidity under tray

The data collected and interpreted with this system will provide information on heat and mass transfer during natural drying; development of harvest schedules for biomass collection systems will also be facilitated. Ultimately, the researchers believe that this measuring modelling will enable them to predict the point at which constant-rate drying ends and falling-rate drying begins.

8.3 Drying in the Pulp and Paper Industry

The pulp and paper industry, as a user of vast quantities of biological materials, water and chemicals; and as a user of variable-sized particles for fuel purposes, has been conducting substantial amounts of research in numerous subfields within the industry. The work in drying includes research at the pulping and pressing segment, and also at the waste product/fuel portion of the operation.

Pulp is a product of wood chips that have been cooked, bleached, and possibly beaten; the material is then pressed to remove the water and produce a dry sheet of kraft. Lengthy discussion of the wet presses, with their felts and rolls nipping the kraft, is not relevant to this study. The techniques that affect water removal may, however, bear examination. Water is the main component of pulp fibre in the water-swollen state; cellulosic fibres in water are sometimes referred to as a "swollen gel" (1982).

The gel water is located in very small pores (a few hundred Angstroms in size). A large amount of water is present both inside the fibre walls and between the fibres. The water is squeezed out from between the fibres, and from the fibre walls themselves, during wet pressing. The re-wetting/drying phenomenon seen in other materials is also seen in pulp; less water is re-absorbed after initial drying of the kraft pulp. Drying during the kraft process is primarily a squeezing and heating procedure.

Waste products in the pulp industry, however, are now being used or seriously examined for use as energy sources. A detailed understanding of the drying of small particles of wood is, therefore, very important; particle drying is significant in regard both to ignition and to particulate emission. Recent work conducted and published by Dorri, Emery and Malte, of the Department of Mechanical Engineering, University of Washington, Seattle (1983), used the sawdust particles of 0.7 to 2.5 mm, flakes, and planar shavings to develop a theoretical/numerical model of the drying rate. The researchers used a vertical drying tube, supplied with hot vitiated air at 400 to 750 K. Drying instrumentation was an optical dew point sensor, used to measure the local gas humidity at five locations along the tube. The researchers discussed three processes that take place in drying of materials:

1) Moisture transfer within the particle to its surface, with surface moisture removal due to external

convection heat and mass transfer. Capillary flow of liquid is due to internal mass transfer.

2) The second process, increasingly important as the moisture content decreases, consists of:
   a) heat diffusion into the particles
   b) local vaporization of free and bound liquid water
   c) mass transfer of the vapor to the particle surface by diffusion and by gas pressure driven flow.
3) A third process of drying occurs when moisture levels are low, and consists of bound water diffusion in the cell walls.

The researchers state that:

> "the driving force for the internal vapor diffusion and gas pressure driven flow is the diffusion of heat into the particle with a consequent increase in the vapor and total pressures. The heat transfer is complicated by internal convection of heat which can proceed in the opposite direction" (Dorri, Emery and Malte, 1983).

Dorri and associates present their results for drying of rectangular particles, in which they show that a steep moisture gradient exists between the particle surface and the front until the free water vanishes; temperature of the bound water regime continually increases. A nearly constant rate of drying is implied.

Spherical particle drying curves indicate a constant rate of drying until very low moisture levels are reached, at which point there is a sharp decrease in the drying rate. Capillary flow was found to have a marked influence on the drying of spherical particles; particle heat transfer occurs over the entire particle, not just at the ends as in a rectangular particle.

During these experiments, it was found that particles could be dried only partially on a single run; discontinuous drying produced the desired moisture content 30 percent faster than did continuous drying.

The researchers concluded that capillary flow substantially influences local moisture and temperature distributions. After capillary flow slows, drying is dependent on heat flow through the particle, i.e. the movement of the heat front into the wood.

Further work on drying of hygroscopic porous media was carried out by Kayihan, Stanish and Schajer (1984). The objective of these researchers was to develop a tool that would simulate drying behavior enabling them to extend the results obtained in experimental drying investigations, and to assess the impact of variables such as relative humidity, and air velocity, and solid properties such as density and hygroscopicity. The drying phenomenon was seen as a process of simultaneous mass and energy transfer, with all phases in thermodynamic equilibrium at the local temperature.

The experimenters used both wood specimens and a porous ceramic solid to compare and verify their data.

The researchers indicate that their approach represents a substantial advance in the modelling and theory of drying. The mathematical description of the drying process is generalized, and accommodates both hygroscopic and non-hygroscopic materials. They have included both conductive and convective heat transfer; mass transfer by gaseous diffusion and bulk flow of gas and liquid through void space, and by bound water through the solid matrix. A new and unique expression for bound water flux is presented, in terms of temperature and vapor pressure gradients.

One of the researchers of this work, Dr. Mark Stanish, is now with a contract research and development firm, Energy International, in Seattle, Washington. He has conducted further studies relative to the relationship between bound water chemical potential and gas phase diffusion in moisture transport through wood. Results of this recent study have been submitted to the Journal of Wood Science and Technology for publication.

8.4 Conclusion

Theoretical and experimental research is being conducted on drying of both hygroscopic and non-hygroscopic materials, around the world, on a substantial scale. The predominant impetus for improved understanding of drying mechanisms is the cost of energy consumed by the drying process, coupled with the need to dispose of biological waste materials in an environmentally acceptable and energy-efficient manner. Research is being carried out primarily at the universities, frequently with funding provided by private industry such as Weyerhaeuser Inc. in the United States, by federal agencies such as the National Research Council of Canada in this country, and by provincial research agencies with funding sometimes jointly provided by government and private industry. Generally, the research conducted in this field by the universities tends to examine the fundamentals of physics and chemistry, whereas that research undertaken directly by industry is more directly applications oriented.

9.0 CONCLUSIONS

9.1 Study Results

Throughout the course of this study, the project researchers encountered information on work performed in subject areas that, at first glance, appeared to be far removed from that of fuel peat dewatering. Preliminary discussions with researchers indicated widespread lack of knowledge regarding peat - its geographic location, formation, composition, use(s), and chemical structure. Exploration of the subject matter, however, almost invariably brought to light parallels perceived by the interviewee with his or her own specialization.

Queries were made by those being interviewed regarding peat components and behavior; this questioning process frequently identified or clarified areas where insufficient information exists. Subsequent discussions yielded detailed information both on current research in specific subject or industrial fields, and on ways in which that knowledge might best be applied to the peat problem. This report has synthesized the comments and published work of research personnel in Canada and abroad.

The economic downturn following the energy crisis of the mid-1970's has had a strongly detrimental impact on the availability of research funding, with energy-related biomass projects affected to a greater degree than many other programs. This situation emphasizes the need to ensure optimum use of available research monies. The most likely manner in which to fully utilize available resources is through the cross-disciplinary coordination of research work, some of which would be directly peat related, whereas other projects could have spin-off value to peat.

The literature relating to peat consistently documents the variability of the peat material. Considering that situation, it becomes reasonable to anticipate that no one method is likely to be appropriate for the dewatering of all peats. Rather, it may be most feasible to use different dewatering methods on different peats, on peats in different economic/geographic regions, or on peats used as fuel only after being used for other purposes, (i.e. chemical extraction). Similarly, some peats may best be dewatered as a pre-treatment, while others may be best utilized as a fully dewatered end product. Definition and clarification of the "best use" will depend upon the variables of peat constituents, location, and projected use. Adequate dewatering techniques, suited to specific but highly differing conditions, can be developed only with precise understanding of the fundamental principles of water removal from the substance.

This study has brought together information gathered from all scientific and technological disciplines; it clearly identifies the array of information available for the use of peat researchers. Not only have subject fields been identified, but research personnel with expertise in very specific fields have been identified. Assembling a fully comprehensive program of programs and personnel is now the function of national and international authorities.

9.2 Application of Transferable Technology

Research in many disciplines and subdisciplines has been described in the preceding sections of this report. The knowledge held in those fields, and by the subject specialists, can be transferred to research aimed at gaining a better understanding of the peat-water relationship. Each technology described in this report can play an important part in further Research and Development (R&D) efforts on this topic. It is useful to consider where each technology fits in the research project development process; the following figure (Page 109) displays this correlation. Each major technology area is identified on the vertical axis, with R&D project phases on the horizontal axis. For the purposes of this report, the phases of the project are:

- Basic research - efforts to understand and quantify the peat-water relationship.
- Applied research - development adaptation and testing of investigative techniques.
- Exploratory development - efforts to explore possible innovation.

In each case, preliminary priority judgments have been made as to whether use of a particular technology is a Priority 1 item; that is, essential to the advancement of knowledge, or whether it is worthwhile but complementary to the research effort.

APPLICATION OF TRANSFERABLE TECHNOLOGY

	Phase of R&D		
Technology	Basic Research	Applied Research	Exploratory Development
Microbiology			
Microbial Populations	I		
Microbial Innovation			I
Porous Media			
Pore Space Characterization		I	
Pore Size Distribution		I	
Pore Configuration Modelling		I	
Flow Models		II	
Physical Chemistry			
Characterization	I		II
Surface & Interfacial Phenomena	I		
Sorption Phenomena	I		II
Surfactants	I	II	I
Flocculation	II	II	II
Emulsions	I	II	II
Cellulose/Lignin Degradation			
Pretreatment		II	
Microbial Treatment			II
Drying Technology			
Measurement		I	
Modelling		I	
Water Binding Mechanisms			
Detection		I	
Analysis of Role	I		

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